

Influence of the bifunctional triethoxy-vinyl
polydimethylsiloxane (PDMS) coupling mechanisms on the
wood flour and polypropylene matrices to enhance the
properties of wood plastic composites (WPC)

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Abstract

The incompatibility problem in combining the contradicting characteristics of wood and plastic in producing wood plastic composites (WPC) has drawn the attention of using coupling agents. A most interesting group of coupling agents concerns bifunctional siloxanes such as the bifunctional triethoxy-vinyl polydimethylsiloxane (PDMS). The bifunctional PDMS combines a polysiloxane backbone with bifunctional groups such as triethoxy and vinyl groups. These groups are not connected prior to compounding with reactions such as hydrolysis and condensation process as in the case of coupling agents based on anhydride or isocyanate functions. The influence of specially synthesized bifunctional PDMS coupling agents on the performance of composites containing 70% wood flour and 30% polypropylene (WF/PP 70/30) was investigated. Comparison with composites of 30/70 and 50/50 WF/PP composition were made to see whether the PDMS coupling agent could more effectively react with wood or with PP. Composites were prepared by compounding treated or untreated WF and PP in a lab scale twin screw compounder. Flexural strength test, impact test, moisture and water absorption analysis, morphology and microstructure investigation, fourier transform infrared analysis and dynamic mechanical analysis were done to determine the properties of WPCs produced with and without PDMS.

With the support of these investigations the influence of single functionality PDMS containing vinyl functional group, triethoxy functional group or a mixture of 50/50 composition containing vinyl PDMS and triethoxy PDMS compared to the bifunctional triethoxy-vinyl PDMS on the mechanical properties and performance of composites were evaluated. Mechanical properties and performance of bifunctional triethoxy-vinyl PDMS treated composites with low molecular weight, high molecular weight and very high molecular weight were also investigated. The optimum amount of coupling agents ranging from 0.88 wt% to 14 wt% was determined as well. Dicumylperoxide (DCP) was used as the radical initiator for the bonding reaction of the vinyl group of the coupling agents with PP.

It was found that the optimum amount of coupling agent for 70/30 WF/PP is about 1.75%. Composites produced with such amounts of bifunctional triethoxy-vinyl PDMS show the best mechanical properties. Also PDMS with very high molecular weight gave composites with better mechanical properties compared to composites treated with single functional groups PDMS coupling agents or bifunctional PDMS with lower molecular weights. It was rationalized as due to the existence of better interphase bonding between wood and PP when both vinyl and triethoxy that were chemically bonded to the PDMS backbone was used comparing to the single functionality PDMS. Covalent bonding between coupling agent-wood interface through triethoxy reaction with OH-group of wood during treatment and coupling agent-PP interface through the reaction of vinyl group with PP initiated by DCP during compounding might have occurred, thus bridging additional the interfaces of wood and PP. The better adhesion with bifunctional triethoxy-vinyl PDMS compared with the mixture of single functionality PDMS could be explained by improvements

of activation energies and modifications of glass transition temperatures. The microscopic images also showed that a homogeneous microstructure of composite has been produced. However, no significant results observed from FTIR spectrum of the expected covalent bonding between treated wood flour and coupling agent was justified as due to the overlapping of the new C-O-C bonding with the existing C-O-C bonding in wood. This research also revealed that DCP has caused chain scission of the PP chain, lowering the mechanical properties of the final wood plastic composite.

Also the impregnation procedure can have a significant influence on the properties of the composite. Impregnation of wood flour with liquid PDMS prior to compounding was identified to be the best methods of applying the very high molecular weight bifunctional triethoxy-vinyl PDMS compared with spraying of 50% master batch of emulsion PDMS onto the wood flour surfaces prior to compounding and insitu compounding of 50% master batch PDMS compounded in PP. The existence of the bifunctional triethoxy-vinyl PDMS from the treated wood specimens after impregnation in the FTIR spectrum showed that coupling agent might have filled in the cell walls and lumens of the wood flour. Improvements in the mechanical properties of the impregnated wood treated composites observed might be due to the better interface bonding between PDMS and wood generated during impregnation.

As a standard, the properties and performance of very high molecular weight bifunctional triethoxy-vinyl PDMS treated composite were compared with the commercially available composites produced with maleic anhydride-modified polypropylene (MAPP) as coupling agent. The results showed that the mechanical properties, activation energy for the glass transition temperature and the microstructure of 70/30 WF/PP composites of both MAPP and PDMS treated composites were comparable. Nevertheless, higher water absorption was measured for 70/30 WF/PP composites treated with MAPP and PDMS composites compared to untreated composites. It is assumed that this effect originates from ineffective processing and unfinished coupling reaction of PDMS by the lab scale equipment. Also hydrolysis of free sugar during PDMS coupling reaction and a reduced encapsulation on the wood by PP contributes the increase of water absorption. The results of this thesis enable as a conclusion, that very high molecular weight bifunctional triethoxy-vinyl PDMS is an effective coupling agent for 70/30 WF/PP composites. The mechanical properties and the performance characteristics of the composite produced can be significantly improved by the use of this coupling agent but the influence of the processing and the treatment methods has to be considered as well.

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List of Abbreviations

ABS	Acrylonitrile butadiene styrene
ATR-FTIR	Attenuated total reflection - fourier transform infrared analysis
Bif	Bifunctional triethoxy-vinyl PDMS
BPO	Benzoyl peroxide
BPP	50% master batch polypropylene
DCP	Dicumylperoxide
DIC	Diisocyanatohexane
DMA	Dynamic Mechanical Analysis
EDX	Energy dispersive X-ray spectroscopy
em-Bif	Emulsion bifunctional triethoxy-vinyl PDMS
FTIR	Fourier transform infrared analysis
HDPE	High density polyethylene
HIPS	High impact polystyrene
HMDIC	Hexamethylene diisocyanate
LDPE	Low density polyethylene
LLDPE	Linear low-density polyethylene
long-WP	Wood particle sizes 1.25 mm – 3.15 mm
MA-g-PE	Maleic anhydride -grafted polyethylene
MA-HDPE	Maleic anhydride -modified high density polyethylene
MAPE	Maleic anhydride-modified polyethylene
MAPP	Maleic anhydride-modified polypropylene
MDF	Medium density fibreboard
MDI	Methylene diphenyl diisocyanates
MFI	Melt flow index
mid-WP	Wood particle sizes 0.6 mm – 1.25 mm
MMS	Methacryloxymethyltrimethoxy silane
MPS	Methacryloxypropyltrimethoxy silane
m-TMI	m-isopropenyl- α,α -dimethylbenzyl-isocyanate
<i>MU</i>	Mass uptake
PDMS	Polydimethylsiloxane
PE	Polyethylene
PEEK	Polyetheretherketone
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinylchloride
PVC-U	Polyvinylchloride-Un-plasticised
SEM	Scanning electron microscopy
TDI	Toluene diisocyanates

UP	Unsaturated polyester
UV	Ultraviolet
WF	Wood flour
WPC	Wood plastic composites
WPG	Weight percent gain

List of Symbols

d	Dimension
E'	Storage modulus
E''	Loss modulus
E_a	Activation energy
f	Rate constant / test frequency
f_o	Frequency factor
m	Mass
R	Ideal gas constant (8.314 J/(mol K))
T	Temperature
$\tan d$	Loss tangent
T_g	Glass transition
T_{II}	Movement of coordinated segments in the amorphous phase
T_m	Melting temperature
T_α^*	Crystallites slippage transition
T_β	Beta transition
T_γ	Gamma transition
w	Weight

1 Introduction

Composites are the most advanced and adaptable engineering materials known to man. They are defined as materials made of two or more components and consist of two or more phases that can still be distinguished when examined under optical or electron microscopes (Nielson & Landel, 1994). Actually, we have been using different types of composite materials in our daily lives without realizing them. These materials can be easily found around us. They normally occur naturally such as many tissues in the body, which made up of stiff fibres such as collagen embedded in a lower stiffness matrix. The material, in which the fibres are embedded, is called the matrix, while the fibres are called the reinforcement. Teeth, plant leaves and bird feathers are also the examples of natural composites. On the other hand, there is as well a wide variety of man-made composites constructed of plastic matrices with organic, inorganic or natural fibres, metal matrices with metal fibres, ceramic matrices with metal or ceramic fibres and so on. Shower stalls and bathtubs made of fibre glass, carbon or epoxy bicycle, and graphite tennis or badminton racket are examples of the products from man-made composites. Those composite materials can be classified in many ways depending on the ideas and concepts to be identified. According to Hull (1995) composite materials can be classified as follows:

- Natural composites for materials such as wood, bone, bamboo, muscle and other tissues.
- Microcomposites for materials such as metallic alloys, for example, steels and also materials such as toughened thermoplastic, for examples, high impact polystyrene (HIPS) and acrylonitrile butadiene styrene (ABS).
- Macrocomposites for engineering products such as galvanized steel and reinforced concrete beams.

Microcomposites as referred to Nielson & Landel (1994) can be divided into three general classes that are:

- Particulate-filled composites consisting of a continuous matrix phase and discontinuous filler phase made up of discrete particles. Examples of this type are wood particles and silica or clay filled plastic polymer composites.
- Fibre-filled composites consisting also a continuous matrix phase embedded with short or long fibres reinforcement as the discontinuous phase. Glass, carbon fibre or Kevlar reinforced plastic polymer are example of this type.
- Skeletal or interpenetrating network composites consisting of two continuous phases. This type includes filled open-cell foams and sintered mats or meshes filled with some material.

Composites can be processed by mixing the separate materials. The dispersion of one material in the other can be done in a controlled way to achieve optimum properties. The ability in processing composites makes them useful and better than their constituent materials. Their utilities often combine the attributes of their individual component. The properties are normally superior or unique in some specific aspect related to the properties of the constituent components (Hull, 1995). They can be tailored for various reasons such as better stiffness, higher materials strength, better dimensional stability, better impact or toughness, higher heat distortion temperature, better mechanical damping, lower gases or liquids permeability, weight reduction, electrical properties or cost reduction.

A simple example of producing composite material is when a metal with high conductivity and a plastic that is electrically insulating are combined in alternating layers in a laminate. A highly anisotropic composite that has the conducting properties of the metal in directions parallel to the layers and the insulating properties of the plastic normal to the layers is obtained (Milton, 2004). Another example is wood that is strong in the fibre direction, but the fibres pull apart easily. By alternating layers of wood that are strong perpendicular to each other, plywood that is strong in two plane directions is obtained (Milton, 2004).

1.1 Wood Plastic Composites (WPC)

Wood plastic composites (WPC) are generally composite materials made of wood based fibres or flour and a plastic polymer. They cover a wide range of composite materials that use plastics such as polypropylene, polyethylene, polystyrene, polyvinylchloride and so on for the matrix phase and fillers ranging from the wood flour to natural fibres. Though both wood and plastics are polymer based, they are very different in origin, structure and performance. The plastic matrix will form continuous phase surrounding the wood component (Clemons, 2008). The WPC will consist of both wood and plastic features. These products are applied in various sectors, including automotive, building and furniture or household articles (Danyadi *et al.*, 2007). WPCs have many benefits and are also environmentally friendly because:

- Residual wood (e.g. sawdust) and recycled plastic could be used beside the virgin wood flour or fibres and plastic polymer.
- Potentially recyclable since it can be reground and reprocessed.
- Most of WPCs are considered non-hazardous waste and can be disposed by standard methods.

Using waste wood products to produce WPC will save the cost of disposal while recycling plastics is also profitable and ethical. The plastic can be from recycled plastic bags or battery case materials, although in demanding applications new plastic materials are required. Producing WPC requires plentiful of raw materials, turning the wood waste and recycled plastic to assets instead of liabilities. WPCs are competitively priced and are competitive with traditional materials such as

timber, MDF and PVC-U (Tangram, 2002). They are easily produced and fabricated by standard processing procedures and are available in a broad range of finishes and appearances. They can be extruded or injection moulded which maximizes resource efficiency and allows design flexibility for improved fastening, stiffening and reinforcement, finishing and joining. These wooden products need no further processing while weather and water resistance make them ideal for outdoor applications where untreated timber products are unsuitable (Kent, 2005). The following figures show some of the products made with WPC.

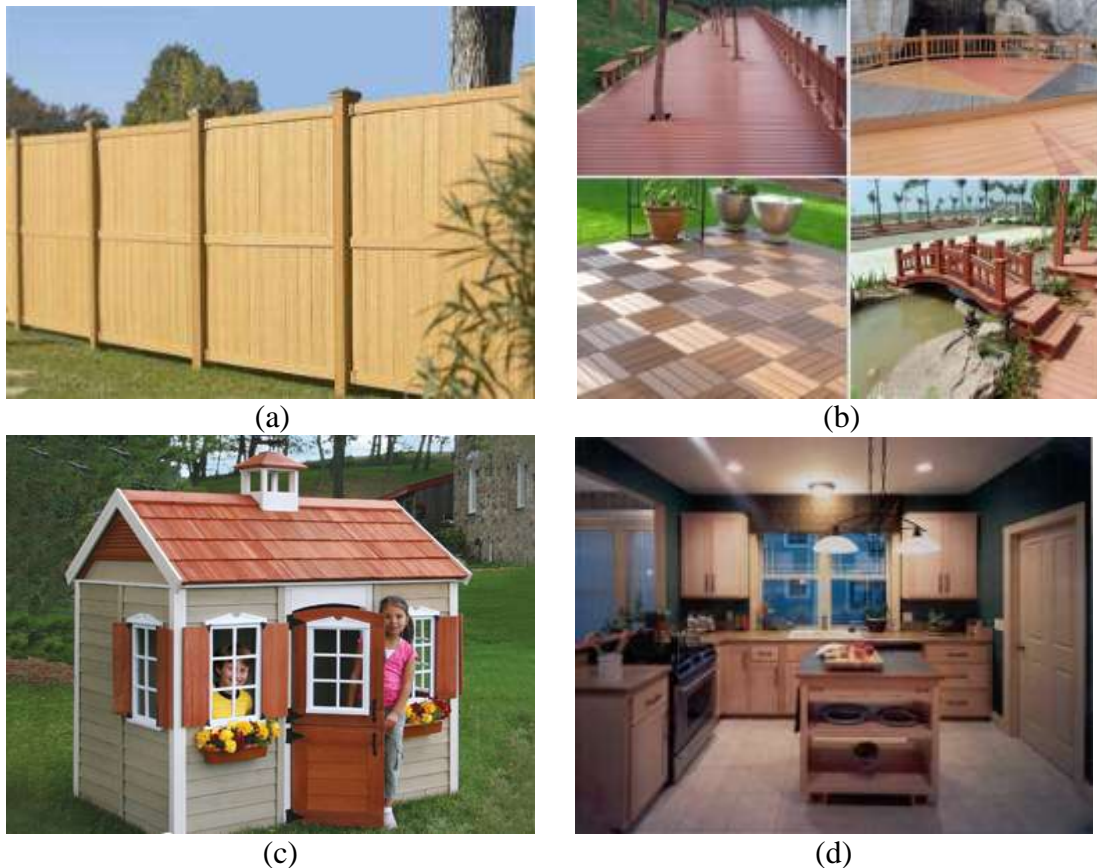


Figure 1.1: Some products made with WPC (a) fencing (b) decking (c) kid playhouse (d) furniture

Combination of wood and thermoplastics results in materials with unique physical properties. In general, the wood component tends to increase the stiffness, thermal stability, UV resistance and workability of the composite. The thermoplastics otherwise improve moisture resistance, resistance to biological decay and impart thermoforming characteristic (Wolcott, 2001). Though their stiffness and strength still lay between both materials the density is generally higher than either. Their properties come directly from their structure; at low filler content, they are intimate mixes of wood particles and plastic. The plastic effectively coats the wood particle as a thin layer (Tangram, 2002). Their properties and characteristics lay more to plastic. Otherwise at higher filler content up to 70% of wood, results in products those are normally stiffer and emulate the characteristic and properties of wood.

Wood and natural fibres offer more advantages over conventional reinforcement materials in plastics. From a polymer composite standpoint, wood is less expensive, stiffer, and stronger than many commodity synthetic polymers, making it a candidate for filling or reinforcing them (Clemons 2000). It is also lighter, less abrasive, renewable and readily available. Its specific properties are comparable to those of other conventional materials used (Saheb & Jog 1999; Clemons 2000). The advantages of WPC have been touted by the researches for a long time. However, these materials were only commercialized and become the cutting edge in the area of building, construction and furniture about two decades ago and as well expanded to the automotive application recently (Niska & Sain, 2008).

The most common reason for the historically low use of WPC is perhaps the unfamiliarity of the new materials in the past, which are very different from the both main constituents polymer in characteristics, structure and performance. Even though the WPC or natural fibre plastic composites consist of both lignocellulosic and plastic material, their characteristics represent neither cellulose nor plastic properties. It took time for both wood and plastic industries to take action of the advantages of the new materials because they knew little about each other. They have few material and equipment suppliers in common and often process materials very differently and on different scales (Clemons, 2000). However, with the improvements in manufacturing processes, equipment design, developments of new analytical and testing methods and growth in process formulation and product design the uses of wood and natural fibre in composite has caught much more intensions in both industries and could potentially replace inorganic fillers as reinforcement in thermoplastic (Niska & Sain 2008; Clemons 2000). Furthermore, the concern and critical discussions on preservation of natural resources and recycling in the late 90's has raised the awareness and changes the interest to natural material with the focus on renewable raw materials and enlarged the focus of research and investigations of wood and natural fibre composites (Bledzki & Gassan 1999).

As explained earlier, the main constituents in WPC are both polymer-based materials yet they are very different in origin, structure and performance. Wood contains polymers such as lignin, cellulose and hemi celluloses those are strongly polar materials and hydrophilic in nature, whereas plastics are very high molecular weight materials whose performance are determined by its molecular structures and are non-polar and hydrophobic in nature (Clemons, 2008; Bledzki & Gassan, 1999; Saheb & Jog, 1999). These contradict characteristics give drawbacks, which are the incompatibility problems in combining these materials and the tendency to form aggregates. Thus the incompatibility of wood and plastic also comes from the very weak interfacial interactions between both components because of the small surface free energy of wood filler compared to the plastic polymer.

The compatibility and homogeneity of wood-plastic components are very well known to be a challenge in producing high-quality wood polymer composites (WPC). This is because the properties of composite materials are strongly determined by the interaction of individual constituents (Hull, 1995). A good surface interaction is very prominent in producing a high quality composite material. In the

case of WPCs, the mechanical properties of the wood component are not only dependent on the fibre or particle properties, but also to the level of adhesion between the wood fibres or particles and the plastic matrix. The interphase formed from the surface adhesion plays an important role in the stress transfer from the matrix to wood particle that contributes toward the performance of the composite.

Mixing and coupling the two constituent components have always been the most interesting subject of investigation in the composite world. Although a lot of research and investigations have been done thoroughly for decades, new findings in improving the performance and characteristic of the WPC are needed to widen the application. On top of that, the uses of WPC are currently so fast developing and expanding in various areas and becoming a very important base material in wood and plastic industry. The increasing demand of WPC industry has been projected to rise from 2009 through 2014 especially in automotive and building materials such as decking, fencing, door and window (LeGault, 2009; Goldsberry, 2009; Carus, 2011). Good adhesion and interaction between both components in producing WPC is essential to achieve good product properties. This is a special problem in WPC production with hydrophobic matrix polymer and hydrophilic wood particle. Adhesion and interaction must be improved to manufacture products of high-quality applications.

1.2 Motivation for research

The problem in combining the two incompatible components, which have opposite polarities or different hydrophilic-hydrophobicity characteristics is the biggest issue we are dealing with, in order to achieve a remarkable performance of WPC. Investigations with silanes have been proven to work well in coupling the wood and plastic to perform better. Silane coupling agents contain three alkoxy functional groups for coupling with the wood. However, before the coupling reaction takes place, the alkoxy silane will need to go through a hydrolysis and condensation process that requires certain condition and time to occur. Using a specially synthesized bifunctional polydimethylsiloxane (PDMS) coupling agent is expected to instantly bridge the interface of both components in the composite and improve the interphase.

1.3 Research Objectives

The main objective of this doctoral thesis is to enhance the performance of the WPC containing 70% wood and 30% polypropylene plastic (by weight) (70/30 WF/PP) by creating better interphase bonding between the incompatible cellulose and PP surfaces. In accomplishing this goal, the following specific objectives were addressed:

- To modify and treat the wood flour using PDMS containing vinyl or/and triethoxy group(s) as a single functional PDMS or as a bifunctional PDMS coupling agent.
- To determine the influence of different coupling agent conditions, that is, the functional group, molecular weight, the materials state and methods of application in producing composite on the WPC performance.
- To investigate the interfacial interaction between wood and plastic matrices under the influence of bifunctional triethoxy-vinyl PDMS coupling agent.
- To evaluate the performance of bifunctional PDMS treated WPC with the influence of wood particle size, wood-matrix compositions and re-compounding process.
- To characterize the mechanical properties of WPC coupled with bifunctional PDMS by the comparison with maleic anhydride-modified PP (MAPP) coupled composite.

1.4 Significance of the study

The findings obtained from this thesis will help to a better understanding of the roles played by PDMS at the interface. It should increase the choice of coupling agent and wider the field of WPC application as well.

1.5 Outline of thesis

This thesis contains 10 chapters. Chapter 1 gives a preliminary introduction to the WPC in which the understanding of the WPC and the composites in general, the compatibility challenge, motivation for research, objectives, significance of the study and outlines of the thesis are presented. Chapter 2 gives a literature review and defines the background of research. The details on the raw materials, the role of the coupling agent and the processing tool are explained. Chapter 3 describes the used materials and methods. In Chapter 4 the investigation on the optimum amount of the coupling agent needed in enhancing the performance of WPC are shown. It was done using commercially available single functionality PDMS containing only vinyl functionality or only alkoxy functionality and also the mixture of both single functional PDMS and the specially synthesize bifunctional PDMS with different molecular weight. The optimum result with MAPP is as well presented. In Chapter 5, the influence of dicumylperoxide (DCP) as a radical initiator in bonding reaction between vinyl group and PP polymer in the WF/PP system itself is explained. The most optimal concentration of DCP to be used with the bifunctional PDMS coupling agent is determined. In Chapter 6 the effect of functional group and coupling agent molecular weight on the performance of WPC are discussed. In Chapter 7 the quality of very high molecular weight bifunctional triethoxy-vinyl PDMS as a coupling agent is revealed. Comparison on performance of the bifunctional PDMS treated WPC and the industrial established MAPP treated WPC is made. Chapter 8 presents the effect of treatment conditions and matrix composition on WPC properties. In Chapter 9 the other factors of interest in influencing the performance of very high

molecular weight bifunctional triethoxy-vinyl PDMS and MAPP treated WF/PP composite are evaluated. Chapter 10 is reviewing the results of the aforementioned studies with the optimum formulation, treatment conditions and the best performance as well as suggestions for future work.

2 Literature review and background of research

The unique characteristic of WPC comes from the two main constituents' components that are wood and plastic, while the compatibility and adhesion contributed by the coupling agent used. To gain better understanding on the properties of WPC, it is an advantage to know the basic structure of the individual component and the theoretical aspects of interaction that might have occurred during processing and production of the WPC.

2.1 Wood flour, the raw material in WPC

Wood physically composes of hollow, elongate, spindle-shaped cells called tracheids or fibres that are arranged parallel to each other along the trunk of a tree (Miller, 1999; Clemons, 2008). These cells form the structural elements of wood tissue. They are various in sizes and shapes and are quite firmly cemented together. The characteristics of these fibrous cells and their arrangement affect the properties such as strength and shrinkage as well as the grain pattern of the wood (Miller, 1999; Clemons, 2008).

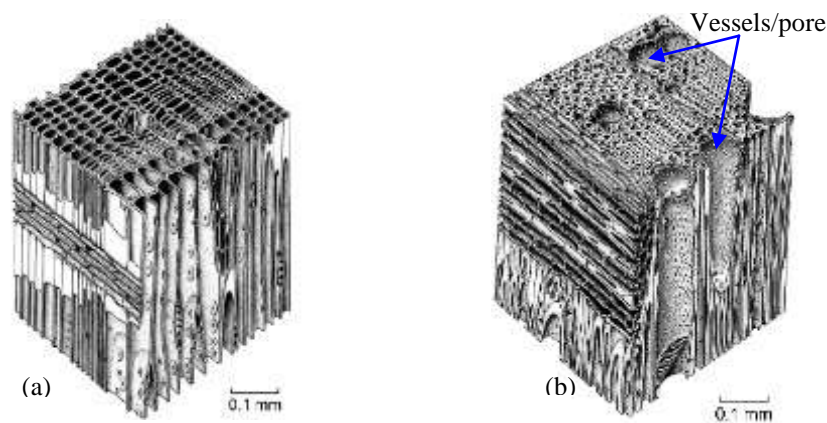


Figure 2.1: The anatomy of wood. (a) Schematic of softwood and (b) Schematic of hardwood (Clemons, 2008).

Wood is grouped into two classes, which are softwood or gymnosperms and hardwood or angiosperms. Softwood normally describes species from conifer trees such as spruces, firs, pines, cedars and yews while hardwood comprise species such as maples, ashes, beeches, cherries and oaks. Softwood is not necessarily softer than hardwood but hardwoods have a more complex structure than softwoods. The main

difference between them is the presence of pores or vessels in the hardwood that is a kind of cell with a relatively large diameter (Sjöström, 1981; Miller, 1999). These cells form the main conduits in the movement of sap. Softwoods do not contain vessels for conducting sap longitudinally in the tree; this function is performed by the tracheids (Miller, 1999). Figure 2.1 shows the different anatomy of hard and softwood (Clemons, 2008). The length of wood fibres for both wood types is also different. Normally, the fibre length of hardwood is in the average of 1 mm. For softwood a value in the range of 3-8 mm is typical and their fibre diameters are typically 15-45 μm .

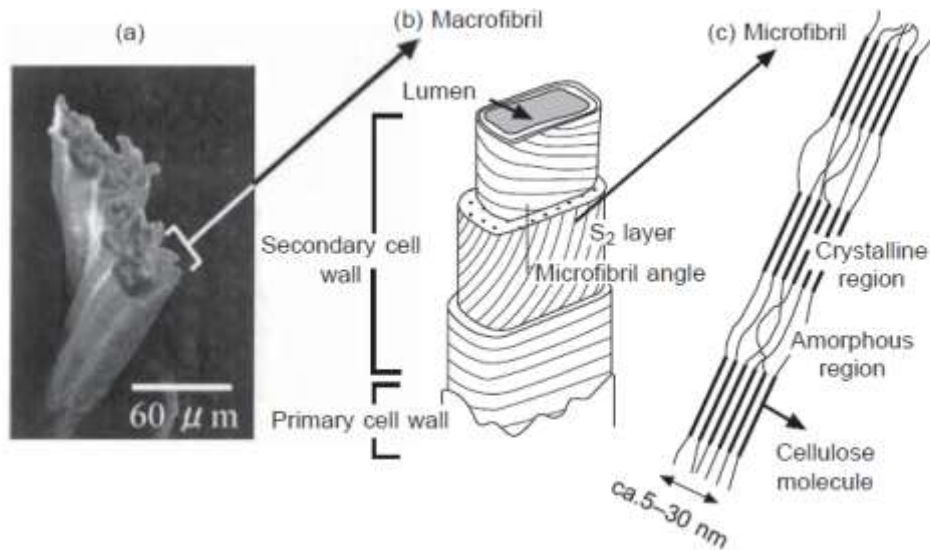


Figure 2.2: (a) Scanning electron micrograph of a wood fibre, (b) Schematic representation of macrofibril and (c) Schematic representation of Microfibril of natural plant (Nishino, 2004)

Chemically a wood cell is composed of 40 to 50% cellulose, 25 to 35% hemicellulose, 15 to 30% lignin, and minor amounts (5% to 10%) of extraneous materials (Miller, 1999; Klyosov, 2007). Figure 2.3 to 2.5 show the chemical structure of the cellulose, hemicellulose and lignin. Cellulose and hemicellulose are polysaccharides. Cellulose has a highly regular structure. It is also a highly crystalline polymer (60-90% crystalline by weight) made up of thousands of glucose residues, and covalently bound “head-to-tail” while hemicellulose are branched chain, low molecular weight polymers composed of several different kinds of pentose and hexose sugar monomers (Miller, 1999; Klyosov, 2007). Cellulose and hemicellulose together will form the plant cell wall. Lignin is an amorphous and a three dimensional linked phenylpropanol polymer often called the cementing agent that binds individual cells together. Lignin is also known to have a highly engineered chemical structure (Miller, 1999; Klyosov, 2007). Hydroxyl groups are responsible for cohesion between those three major components of the wood cell wall and for sorption of moisture. However, compared with cellulose and hemicellulose, lignin is less hydrophilic (Piao *et al.*, 2010). Figure 2.2 shows schematically the location of the cellulose molecules in a wood fibre.

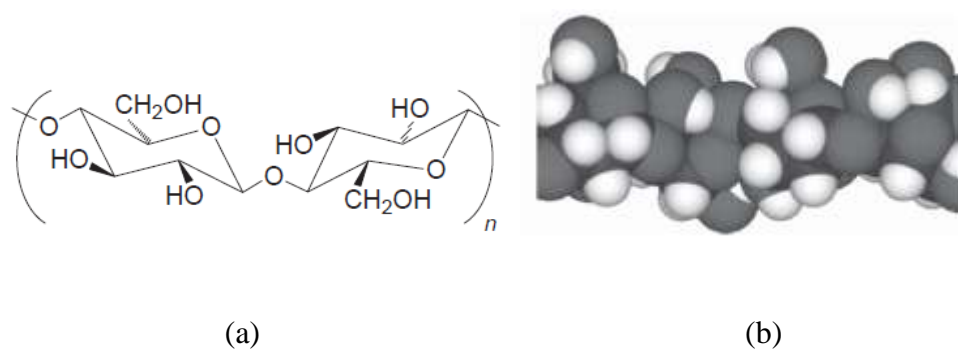


Figure 2.3: (a) Block of two glucose molecules in cellulose that is repeated thousands of times to make a more or less complete cellulose chain. Bundles of those chains form a cellulose fibre. (b) A three-dimensional model of the same block of two glucose molecules (Klyosov, 2007).

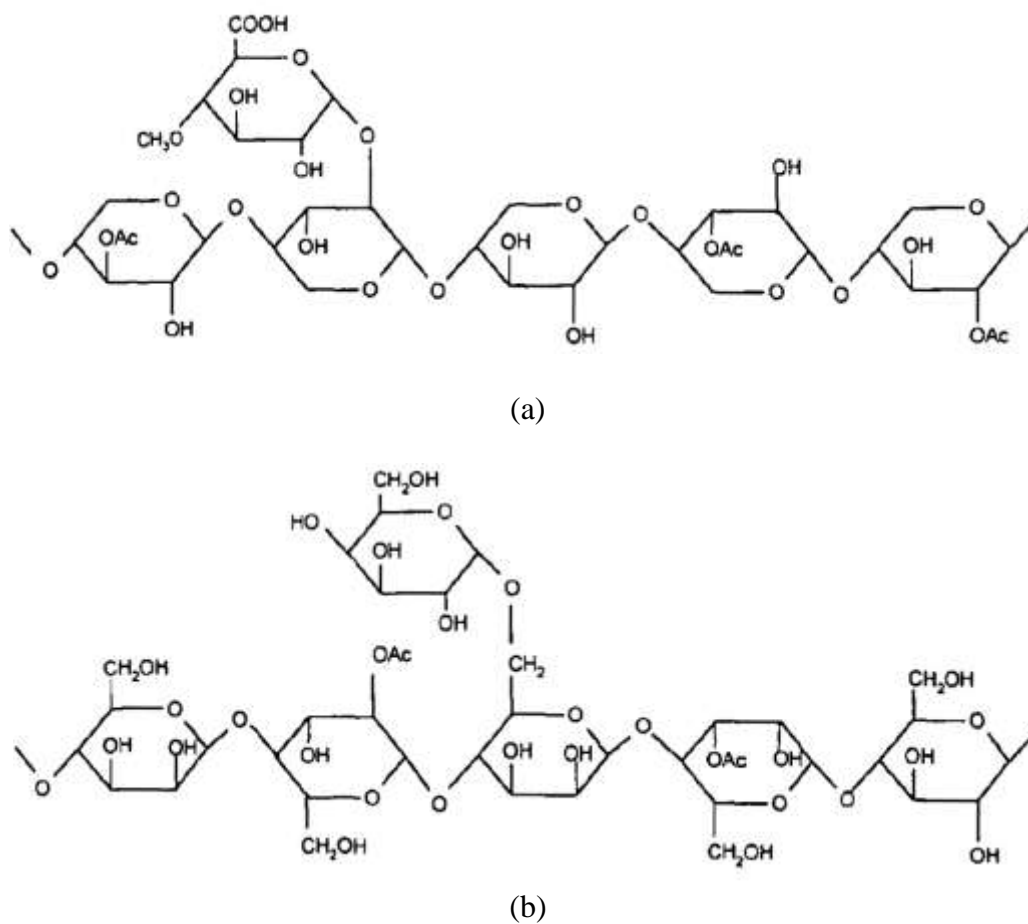


Figure 2.4: Chemical structure of hemicelluloses (a) O-acetyl-4-O-methylglucuronoxylan from hardwood and (b) O-acetyl-galactoglucomannan from softwood (Baeza & Freer, 2001)

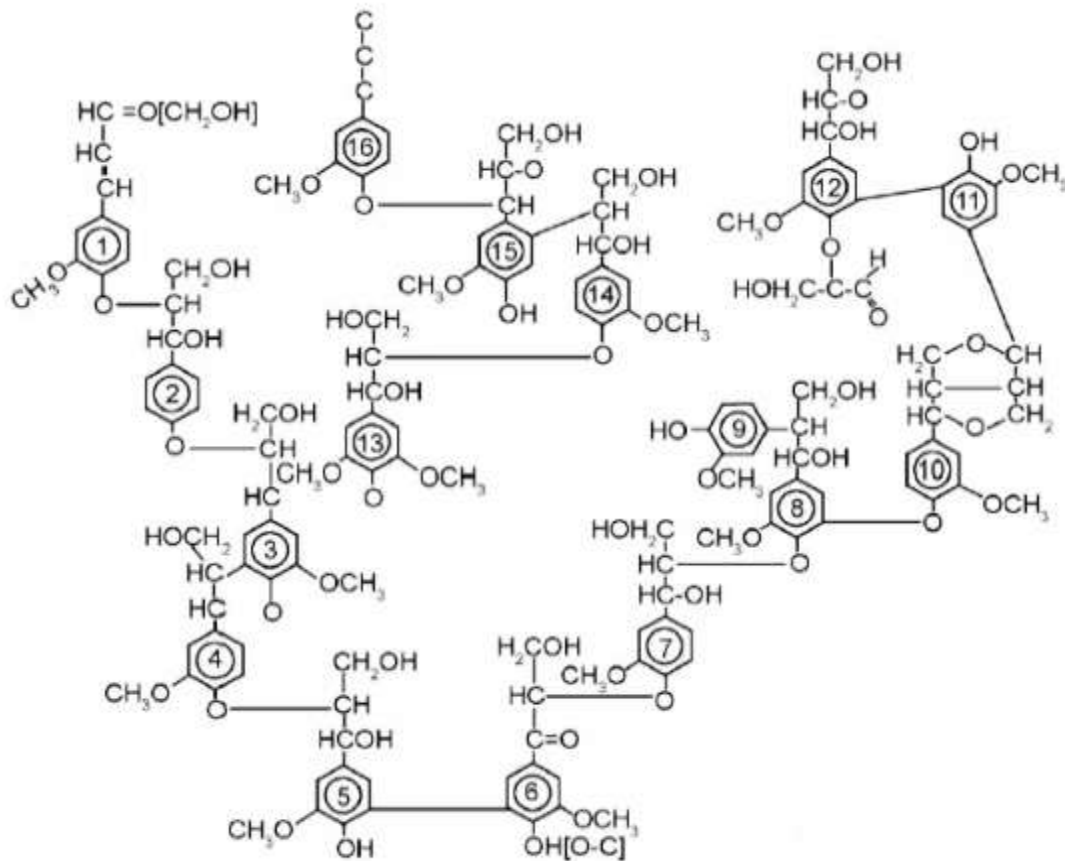


Figure 2.5: Chemical structure of softwood Lignin (Baeza & Freer, 2001)

Wood in term of fibres or flour is used as filler and reinforcement of plastic. WPC usually contains between 30 and 70 percent of wooded particulates and fibres. There are various ways of producing filler and reinforcements from wood to be used in the plastic composites. However, most commercial methods result in either some type of fibre or particulate (Clemons, 2008). Wood in particle form that is small enough to pass through a screen with 850-micron openings or 20 US standard mesh is known as wood flour (Clemons & Caufield, 2005). This type of wood comprises bundles of fibres rather than the individual fibres. Wood flour has been produced commercially since the beginning of the 20th century and has been used in various products, including soil amendments, extenders for glues and absorbents for explosive. One of its earliest uses in plastic was in phenol formaldehyde and wood flour composite called Bakelite (Clemons & Caufield, 2005).

Wood flour is derived from various scrap woods from the wood processor. High quality wood flour must be of a specific species or species' group and must be free from bark, dirt and other foreign matter (Clemons & Caufield, 2005). Normally wood flour is made based on the regional availability of clean raw materials from wood processing industries. The species' selection normally bases on many reasons such as slight colour differences, regional availability and familiarity (Clemons & Caufield, 2005). The most commonly used wood flour for plastic composites are from pine, spruce, oak and maple. Although there is no standard of producing wood

flour, the main aim is the reduction in size and size classification. The mostly commercialized wood flours used as fillers in thermoplastics are less than 425 μm or 40 US standard meshes. The finer wood flour will result in a more uniform appearance and smoother finish of composite, however, it will cost also more than the coarser wood flour. Their bulk density is about 190 – 220 kgm^{-3} depending on the moisture content, particle size and species (Clemons & Caufield, 2005). Wood flour is hygroscopic and normally will contain at least 4% moisture when delivered. Once dried, wood flour can still absorb moisture quickly until equilibrium is reached. The moisture absorption depends on the surrounding conditions and is especially affected by temperature and humidity. The following table shows the equilibrium moisture content for wood at different temperature and relative humidity as listed by Simpson and TenWolde (1999) and Clemons and Caufield (2005).

Table 2.1: Equilibrium moisture content for wood at different temperature and relative air humidity

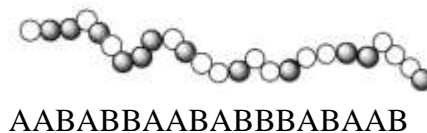
Temperature		Moisture content (%) at various relative air humidity value								
(°C)	(°F)	10%	20%	30%	40%	50%	60%	70%	80%	90%
-1.1	30	2.6	4.6	6.3	7.9	9.5	11.3	13.5	16.5	21.0
4.4	40	2.6	4.6	6.3	7.9	9.5	11.3	13.5	16.5	21.0
10	50	2.6	4.6	6.3	7.9	9.5	11.2	13.4	16.4	20.9
15.6	60	2.5	4.6	6.2	7.8	9.4	11.1	13.3	16.2	20.7
21.1	70	2.5	4.5	6.2	7.7	9.2	11.0	13.1	16.0	20.5
26.7	80	2.4	4.4	6.1	7.6	9.1	10.8	12.9	15.7	20.2
32.2	90	2.3	4.3	5.9	7.4	8.9	10.5	12.6	15.4	19.8
37.8	100	2.3	4.2	5.8	7.2	8.7	10.3	12.3	15.1	19.5

2.2 Polypropylene plastic, the raw material in WPC

Plastic polymer belongs to a chemical family referred to as molecules with high molecular weight. This high molecular weight polymer may be defined as a macromolecule built up by repetition of small, simple chemical units called monomer (Brydson, 1999). These polymers are known as plastic when they contain other materials such as stabilizers, plasticizers or other additives added in them during processing (Clemons, 2008).

There are basically three ways by which plastic polymer may be produced synthetically from monomers. These techniques are addition polymerization, condensation polymerization and rearrangement polymerization. Plastic polymer can contain one type of monomer (homopolymers) or multiple monomers (copolymers, terpolymers, etc.). The arrangement of the repeating unit in the multiple monomers can be controlled during polymerization. The following Figure 2.6 shows some possible ways in which two monomers; A and B can be combined together in one chain as a copolymer plastic (Clemons, 2008).

Random copolymer:



Alternating copolymer:



Block copolymer:

a) Diblock copolymer



b) Multiblock copolymer



Graft copolymer:

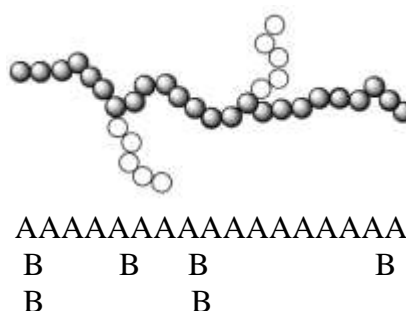


Figure 2.6: Different monomers combination of copolymer (illustrations are from Moad & Solomon, 2006).

Crystalline or amorphous are two common molecular structures in a plastic polymer which are much related in determining the physical and mechanical properties of the material. When thermoplastic molecules remain disordered as they are cooled from the melt, they are considered amorphous thermoplastics. In the amorphous state thermoplastic will have a high concentration of molecular entanglement, which acts like the cross-link in thermoset. When they form regions of highly ordered and repetitive molecular arrangements on cooling, they are known as semi crystalline thermoplastics. In amorphous thermoplastics, heating will lead them to disentanglement and change from rigid solid to a viscous liquid while in semi-crystalline thermoplastics heating will results in melting of the crystalline phase to give an amorphous viscous liquid. There is 40% – 80% crystallinity for such a semi

crystalline thermoplastic. The most commonly used thermoplastics are polyethylene (PE), polypropylene (PP) and polyetheretherketone (PEEK) which are semi-crystalline. Polyvinylchloride (PVC) and polystyrene (PS) are commonly used thermoplastics as well but amorphous. (Hull, 1995; Brydson, 1999). Figure 2.7 shows the schematic representation of the chain folding in crystalline and amorphous part of polymer.

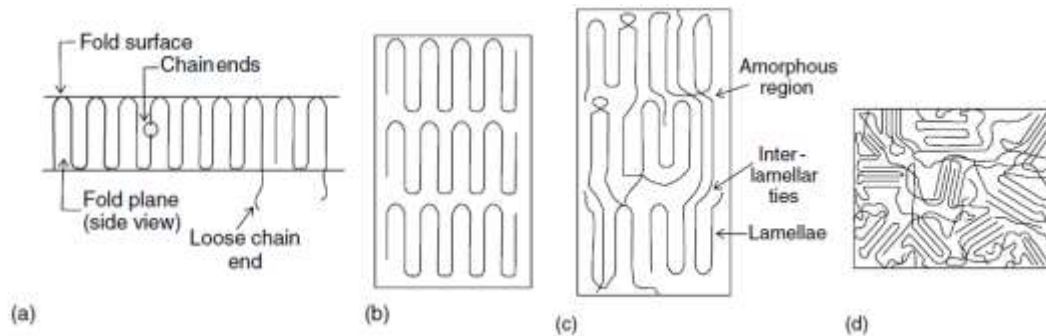


Figure 2.7: Schematic representation of (a) fold plane showing regular chain folding, (b) ideal stacking of lamellar crystals, (c) interlamellar amorphous model, and (d) randomly distributed crystallites (Chanda & Roy, 2006)

Polypropylene (PP) is a thermoplastic polymer, based on the propene monomer (C_3H_6). It is produced by the chemical industry and it is used in a wide variety of applications, such as packaging, textiles (e.g., ropes and carpets), stationery, plastic parts and reusable containers of various types, laboratory equipment, automotive components and other. The special characteristics of PP are:

- High hardness, stiffness, and strength among the polyolefins
- Relatively high dimensional stability under heat
- Low toughness at low temperatures up to approx. 0 °C
- High chemical and corrosion resistance
- Very low water absorption
- Easily machined and cut
- Easy to maintain and clean
- Excellent thermal insulating and dielectric properties
- Long life span

Good balance of properties, which can be tailored to a wide range of fabrication methods and applications and its low cost, make it useful in many different industries and application (Maier and Calafut, 1998).

PP contains a methyl group (CH_3) attached to a carbon chain. There could be several arrangements of the methyl group to the carbon chain, which is known as tacticity. When the CH_3 is attached only to one side of the carbon chain, the PP is known as isotactic. When they are attached on alternating sides of the chain, they are syndiotactic and when they lack a consistent arrangement, then they are known as atactic. Atactic PP is a comparable soft material that is mainly used in applications

such as sealants and caulks (Brydson, 1999). Tacticity not only affects the crystallinity but also induces completely different properties in the polymer. The structural difference results in profound variations in the properties of PP isomers, as shown in Table 2.2 (Chanda & Roy, 2006).

The most commercial polypropylene is isotactic and has an intermediate level of crystallinity between that of low density polyethylene (LDPE) and high density polyethylene (HDPE). Polypropylene has a very good resistance to fatigue and is normally stiffer than some other plastics and reasonably economical. The one to be used in this project is isotactic polypropylene (Figure 2.8) with low MFI having lower flow rate, thus giving better matrix distribution during processing. The isotactic arrangement gives the plastic a better strength and stiffness (Brydson, 1999). Polypropylene is also one of the major commodity plastics, which may be processed below the decomposition temperature of lignocellulosic fibre (about 220 °C) (Bengtsson & Oksman, 2006).

Table 2.2: Properties of PP stereoisomer (Chanda & Roy, 2006)

Property	Stereoisomers		
	Isotactic	Syndiotactic	Atactic
Appearance	Hard Solid	Hard Solid	Soft rubbery
Melting temperature (°C)	175	131	< 100
Density (g/cc)	0.9 - 0.92	0.89 - 0.91	0.86 - 0.89
Tensile strength (N/m ²)	3.4 x 10 ⁷	-	-
Crystallinity (%)	< 70	-	-
Glass transition temperature (°C)	0 to -30	-	-11 to -135
Solubility	Insoluble in most organic solvents	Soluble in ether and aliphatic hydrocarbon	Soluble in common organic solvents

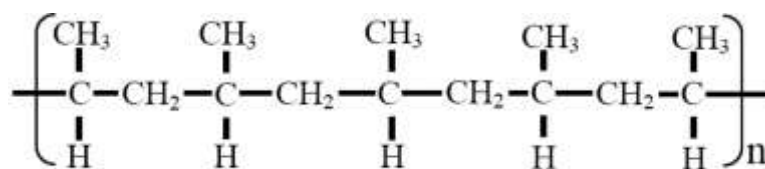


Figure 2.8: Isotactic polypropylene structure (Brydson, 1999).

2.3 Role of coupling agent in enhancing WPC performance

A coupling agent is a substance used, in small quantities, to treat a surface so that bonding occurs between it and another kind of surface such as a mineral or a polymer matrix (Pvitchavd, 1998). This substance, on the other hand, will enhance the adhesive bonding of dissimilar surfaces when it works as an interphase at the dissimilar surfaces' interfaces (Sombatsompop & Chaochanchaikul, 2005). Coupling agents comprise bonding agents and surfactants (surface-active agents), including compatibilizers and dispersing agents (Lu *et al.*, 2000). Bonding agents act as bridges that link wood fillers and the plastic matrices. One or more of the following mechanisms may occur during the linking process: covalent bonding, polymer chain entanglement or strong secondary interactions as in the case of hydrogen bonding, acid-base interaction or electrostatic attraction (Lu *et al.*, 2000; Weissenbach & Mack 2005). Compatibilizers are used to provide compatibility. They act either by reducing the interfacial tension of the immiscible polymers or by lowering the surface energy of the fibre, making it non-polar, more similar to the plastic matrix (Lu *et al.*, 2000). These mechanisms depend on the type of the compatibilizers used. Dispersing agents act at the interface of the wood fibre-matrix. They reduce the attractive forces at the interface. This enables uniform dispersion of wood fibres in a plastic matrix without aggregation and facilitates the formation of an interface (Lu *et al.*, 2000; IUPAC, 2007).

Using a coupling agent in enhancing the adhesive bonding of dissimilar surfaces is known as chemical modification in which a third material is introduced into the system. Coupling agents will improve the compatibility and adhesion between polar wood fibres and non-polar plastic matrices in the WPC system. They can chemically modify the lignocellulosic material, grafting of polymer onto the lignocellulosic material or work as compatibilizers. They are usually used for eliminating weak boundary layers, developing a highly cross-linked interphase region and improving wetting between the polymer and fibre substrate surface (Sombatsompop & Chaochanchaikul, 2005).

The coupling agent used may permanently alter the nature of the lignocellulosic material, so that it is more compatible with the matrix or providing the opportunity for creating covalent links between the lignocellulosic material and the polymer by grafting or will act at the interfacial of both lignocelluloses and the matrix to bond them together. The most studied classes of chemicals in coupling wood-plastic in WPC are anhydrides, isocyanates and epoxides (Hill, 2000). The role played by coupling agent in enhancing the surfaces adhesion and compatibility are very important to ensure better stress transfer between the matrix and filler phases, which is a prominent factor in improving the mechanical performance of the composites (Bengtsson & Oksman, 2006). It is also important to ensure that the coupling agent could result in more uniform dispersion and distribution of wood filler in the plastic matrices in order to avoid crack initiation and failure. The most preferably coupling agent to be chosen is the one that could bridge the interface and form chemical bonding between wood and plastic.

As a summary coupling agent reacts as follows:

- Enhancing the adhesive bonding of dissimilar surfaces
- Bridging the interphase
 - Covalent bonding
 - Polymer chain entanglement
 - Strong secondary interactions
- Creating an interface bonding
 - Increase compatibility
 - Enable uniform dispersion of filler
 - Improve quality of filler/matrix interaction
- Performing better mechanical properties

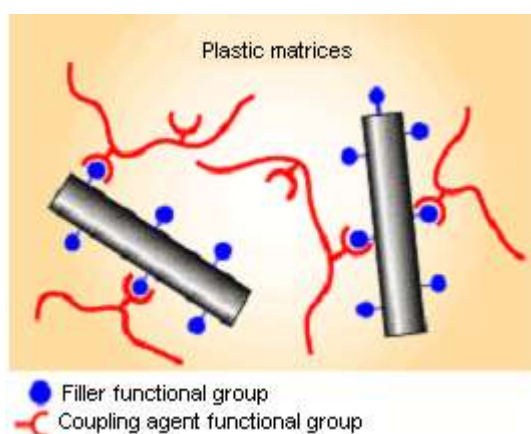


Figure 2.9: Coupling agent reaction (illustration from Specialchem4polymers)

Coupling agents are classified as organic, inorganic and organic-inorganic compounds. Organic agents include isocyanates, anhydrides, amides, imides, acrylates, chlorotriazines, epoxides, organic acids, monomers, polymers and copolymers. For inorganic coupling agents, only silicates are used in WPC and organic-inorganic agents include silanes and titanates (Lu *et al.*, 2000). Organic coupling agents usually have a bi- or multifunctional group that could interact with the fibre to form covalent or hydrogen bonding or modify the polymer matrix by graft biopolymerization or cross-linking at the interface depending on the functional group types and the filler types. Inorganic coupling agents possibly act as dispersing agents and counteract the polarity of wood surface to improve compatibility with the matrix. The organic-inorganic agents are hybrid compounds in structure. They are between organic and inorganic agents in function (Lu *et al.*, 2000).

As for the WPC system, a lot of studies have been done using coupling agents such as silanes, isocyanates, anhydrides or acrylates on the different wood fibre or flour/plastic polymer systems (Raj *et al.*, 1989; Bengtsson *et al.*, 2006; Bengtsson *et al.*, 2005; Ichazo *et al.*, 2006; Hu *et al.*, 2006; Nachtigall *et al.*, 1999). These coupling agents chemically react with the wood surface at one end and on the other

end interact with the matrix to improve stress transfer from the matrix to the wood. Silane and isocyanates are reported to react with OH – groups on the wood surface to form especially primary chemical bonds.

2.3.1 Organic peroxides

Organic peroxides commercially are used as oxidizing, epoxidizing, or bleaching agents, as initiators for radical polymerization, and as curing agents (Reetz *et al.*, 2009). However over two decades ago researchers have reported that peroxides can also work as a coupling agent in grafting the cellulose fibre directly to the polyolefin polymer in a WPC system (Bataille *et al.*, 1990; Sapiuha *et al.*, 1990). Both benzoyl peroxide (BPO) and dicumyl peroxide (DCP) have been used as a pre-treatment for wood fibres by Bataille *et al.* (1990) and to matrix by Sapiuha *et al.* (1990).

Peroxides will go through homolytic decomposition of the covalent bonds by energy absorption to form free radicals. The energy includes almost any form, including thermal, electromagnetic (ultraviolet and high-energy radiation), particulate, electrical, sonic, and mechanical. Free radicals can undergo four general types of reactions: (1) transfer or abstraction, (2) elimination, (3) addition, and (4) combination or coupling. The free radicals react very rapidly thus the initiator must be produced in the presence of the monomer that is to be polymerized (Reetz *et al.*, 2009). It is reported that peroxides had initiated free radicals and reacted between cellulosic fibres and polyethylene matrix systems and grafted them together (Bataille *et al.*, 1990; Sapiuha *et al.*, 1990). Figure 2.10 shows the decomposition reactions of some peroxide to initiate free radical (Bremner & Rudin, 1993).

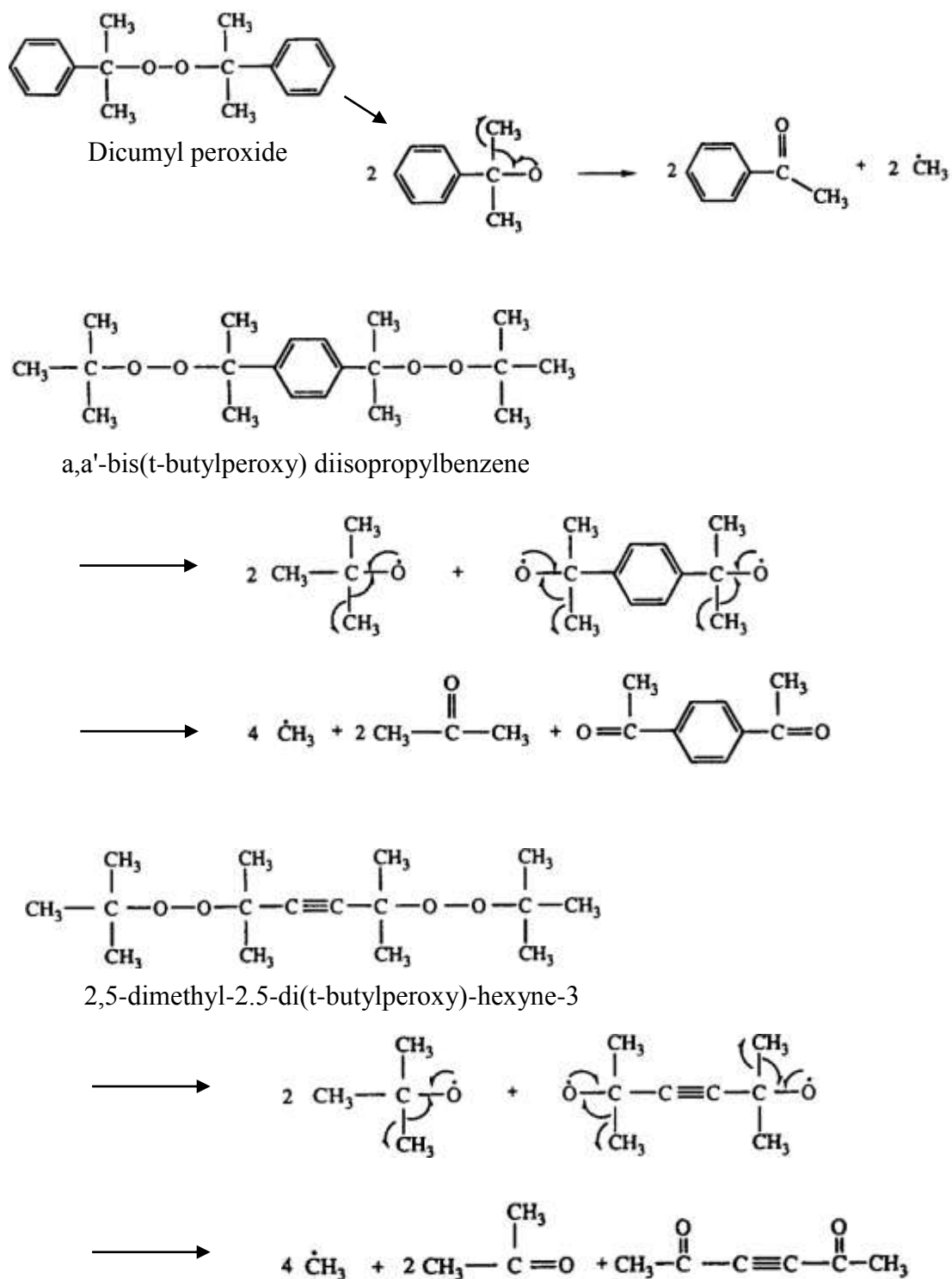
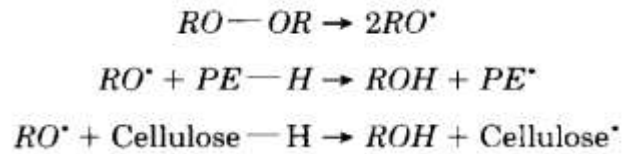


Figure 2.10: The decomposition reactions of some peroxides

The following reaction mechanisms were proposed by Sapieha *et al.* (1990) showing how the grafting of polyethylene to the cellulose fibre takes place and other possibilities of reaction during processing may occur.

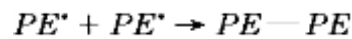
(1) Free radical reaction between PE and cellulose fibres



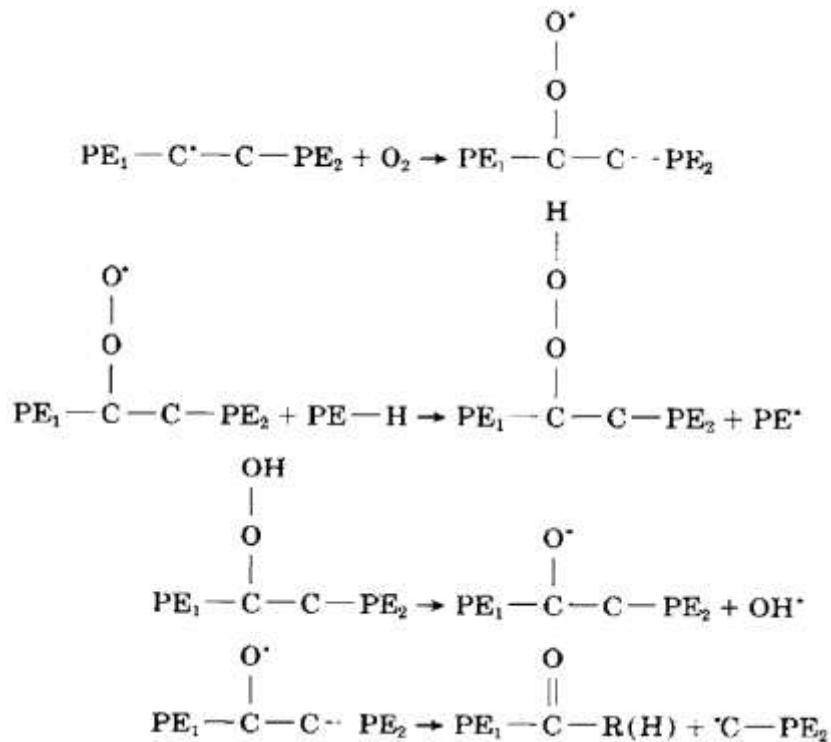
The hydrogen abstraction in cellulose may occur from OH – groups and C-H – groups of the cellulose backbone as well as from methylol (-CH-OH) groups. On the other hand, the hydrogen abstraction for PE may take place at tertiary carbons of the alpha-olephin units because the LLDPE used was a copolymer of alphaolephins (i.e., butene, hexene, and octene) with ethylene.

(2) The following reactions may take place during the processing of composites:

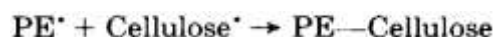
- (a) Increase of molecular weight and crosslinking of the polymer matrix by combining macro-radicals of polyethylene



- (b) Introduction of polar groups (such as acidic and ketonic) into the nonpolar polyethylene chains by oxidative degradation



- (c) Grafting of polyethylene onto cellulose fibres by combining cellulose and polyethylene radicals



Reactions (a) and (c) should lead to increase molecular weight and thus to higher melt viscosities, while oxidative degradation (b) should lead to a decrease in molecular weight. Peroxide concentration plays an important role in the efficiency of these reactions while reaction (c) also depends on the available cellulose surface and, therefore, on the concentration of cellulose fibres.

Even though the peroxides can be used alone as a coupling agent in a WPC system, its application is wider and more reported as a radical initiator in grafting a functional group from other coupling agents to bridge the interface in a WPC system. Perhaps the better performance showed by the grafted coupling agent caused the peroxides preferably to be used as a radical initiator in grafting, not as a coupling agent itself. Examples are to graft anhydride group (Renner *et al.*, 2010; Clemons, 2010; 2007; Ghaemy & Roohina, 2003) or a vinyl group (Bengtsson *et al.*, 2005 & 2006) to a polyolefin. The following reaction (Figure 2.11) shows how DCP initiated the grafting reaction of vinyl functional group from a silane coupling agent to a polypropylene polymer backbone.

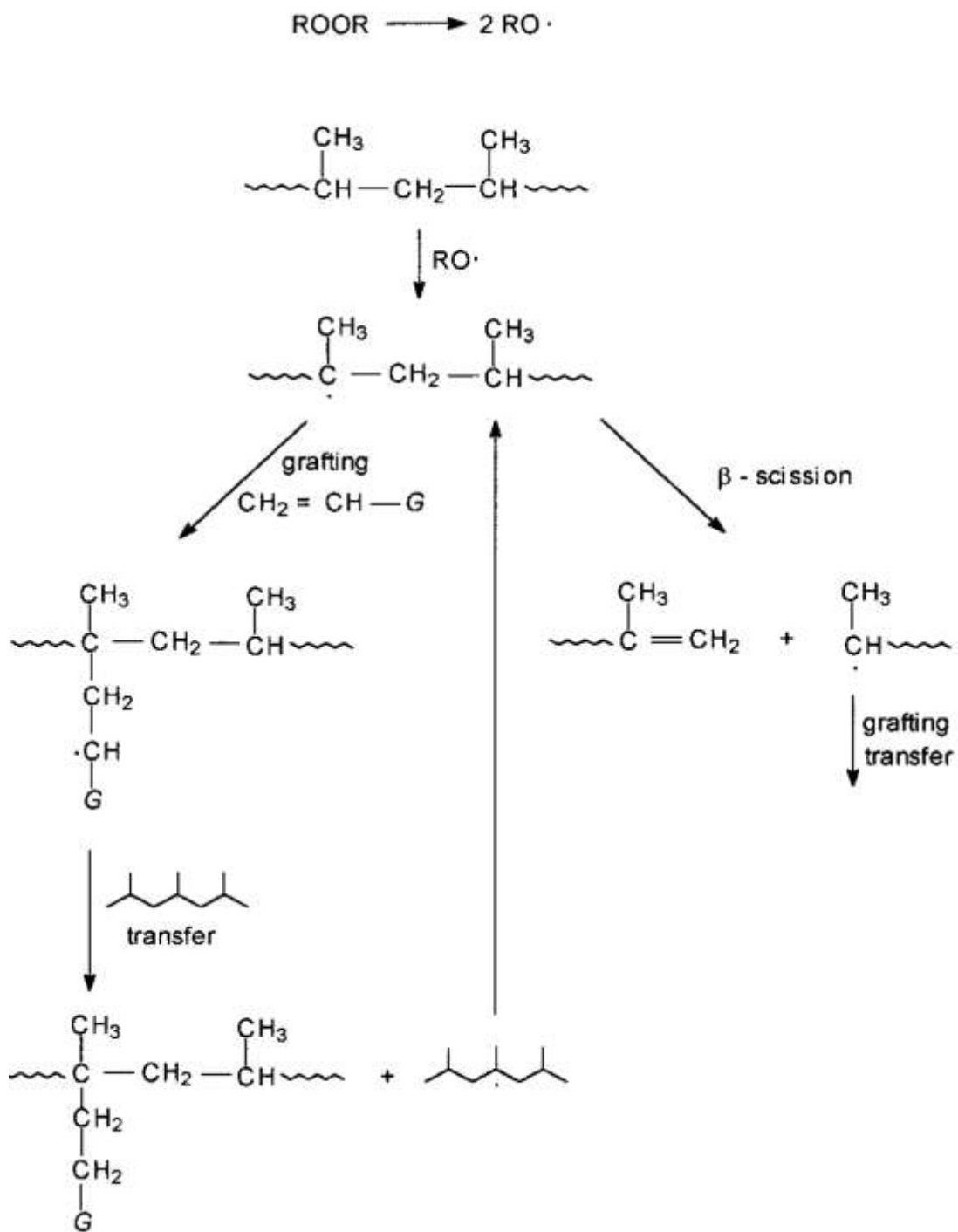


Figure 2.11: Grafting reaction of vinyl functional group from a silane coupling agent to polypropylene (Nachtigall *et al.*, 1999)

2.3.2 Silane coupling agents

Raj *et al.* (1989) used both isocyanates and silane coupling agents in cellulose fibre/linear low-density polyethylene (LLDPE) composites by depositing these molecules onto the fibres from a dilute solution. The fibres were dried before compounding with the plastic in the extruder. They reported better properties with the use of isocyanates as compared with silanes. Strength and ultimate failure strain were improved using either of the coupling agents compared to the uncoupled systems.

During processing, different adhesion mechanisms and interfacial interactions may occur, and they may be in combination of several mechanisms depending on the formulation or coupling agent used. It was proposed by Bengtsson *et al.* (2006) that the following mechanisms (Figure 2.12) might have taken place in WPC when they used vinyltrimethoxy silane as a coupling agent in a wood flour/polyethylene system with DCP as the radical initiator. Acting as a radical initiator, DCP initiated free radicals and performed covalent bondings between wood and PE. It was also suggested earlier by Bengtsson *et al.* (2005) that a siloxane bridge is formed at the wood surface, while the other end of the silane crosslinks with the HDPE.

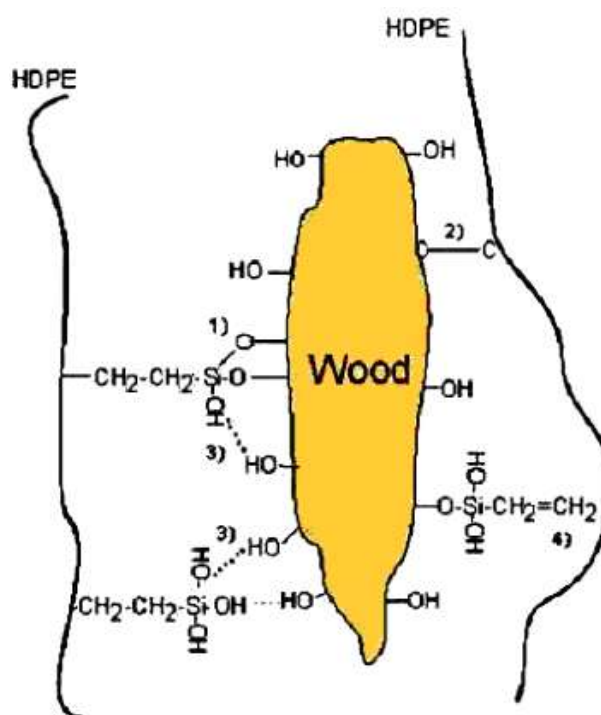


Figure 2.12: Proposed bonding mechanisms in the silane cross-linked composites. Covalent bonding between wood and PE through (1) condensation and (2) through free radical reaction. Secondary interactions through (3) hydrogen bonding and (4) van der Waals interaction Bengtsson *et al.* (2006).

Figure 2.13 shows the reaction mechanism, which has taken place during coupling reaction of alkoxy silane with the surface hydroxyl group of substrate and bridge the composite. Alkoxy silane will have to go through four steps to perform bonding. Initially, hydrolysis of alkoxy groups occurs. After the first and second steps alkoxy groups are hydrolysed. Afterwards condensation to oligomers will follow. The silanol hydrogen is more electrophilic and much more reactive if compared to the hydrogen of a carbinol moiety (Witucki, 1993). This is due to the larger, more electropositive, atomic structure of silicon, which results in a high dipole moment for the silanol group and greater hydrogen bonding. The tendency toward self-condensation can be controlled by using alcoholic solvents, dilution, and by careful selection of pH ranges.

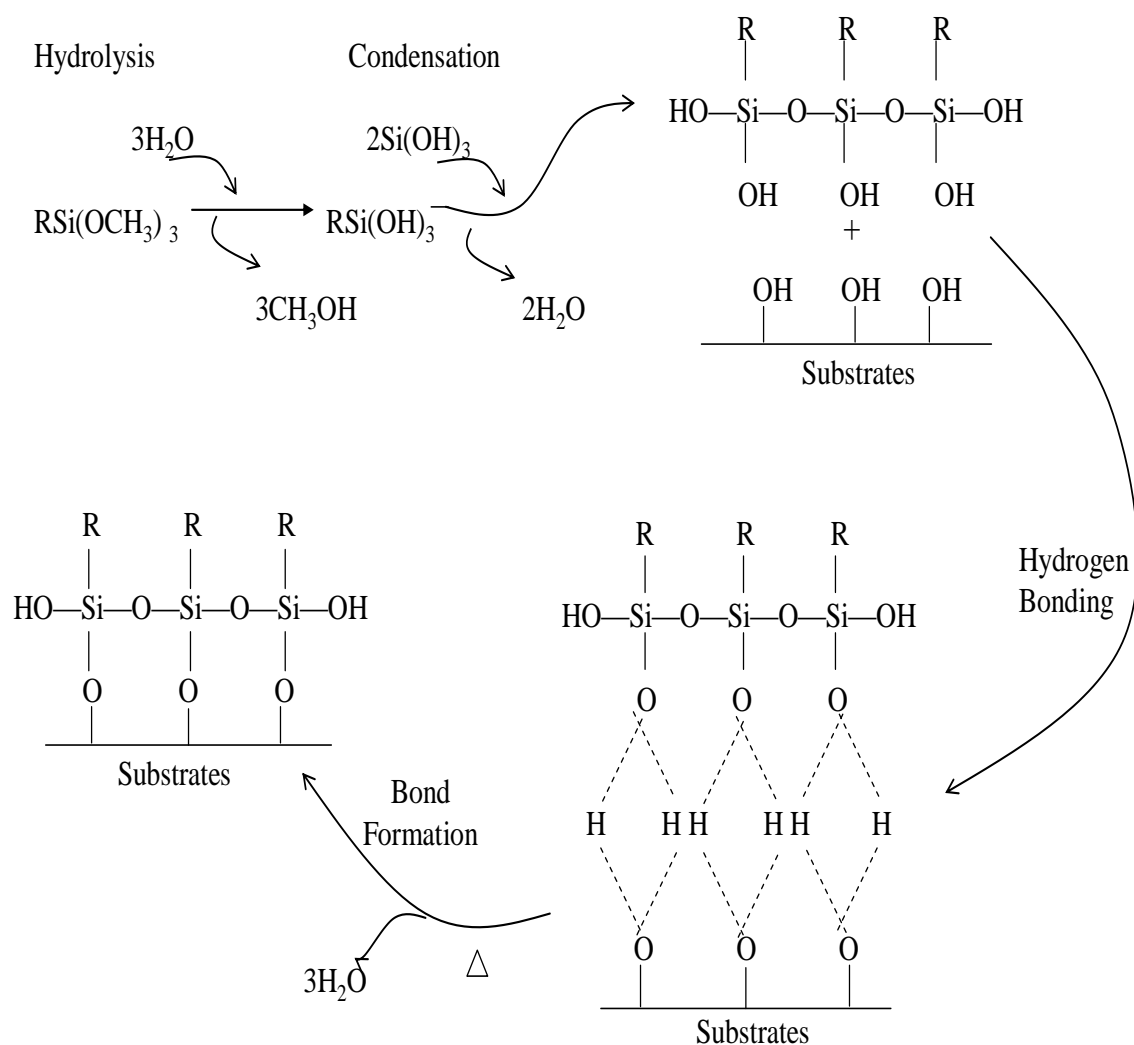


Figure 2.13: Alkoxy silane coupling reaction (Arkles, 2000; Arkles *et al.*, 1992).

As reported by Weissenbach and Mack (2005) and Xie *et al.* (2010), the rate of this hydrolysis depends on the pH value of the hydrolysis medium as well as on the type of organo- and silicon-functional groups. The alkoxy functional group on the silicon compound has a significant influence on the hydrolysis rate. The order of reactivity is as follows: propoxy \ll ethoxy $<$ methoxy. Hydrolysis and condensation rates of silane in different pH ranges can be expected as shows in the following Figure 2.14.

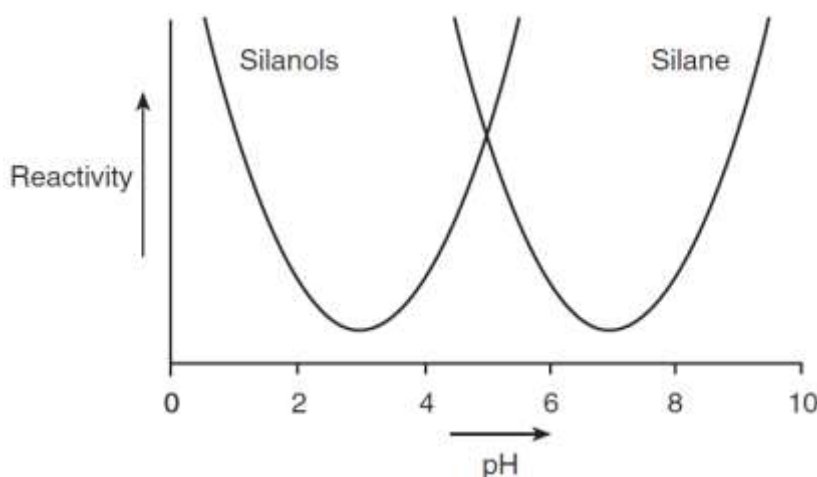
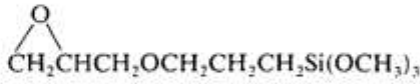
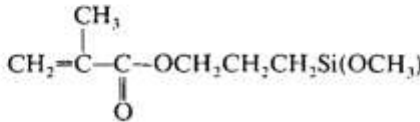
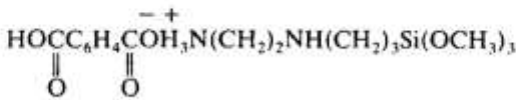


Figure 2.14: Reactivity of silanes and silanols (Weissenbach & Mack, 2005)

According to Weissenbach & Mack (2005), silanols are most stable at around pH 3, and their reactivity is higher at a pH lower than 1.5 or higher than 4.5. Silanols condense to form oligomers and, ultimately, two- and three-dimensional networks. Silanes, on the other hand, hydrolyse very quickly at very low pH. Relatively stable silanols are formed and will form coordinated networks over time. Silanes are most stable at neutral pH thus, hydrolyse very slowly to silanols, which are unstable and condense. Both cases give a slow reaction in the transition from silanes to Si–O–Si networks. At pH $>$ 8, silanes become highly reactive once more and form silanols very quickly. These silanols are very unstable and condense very quickly to give uncoordinated Si–O–Si networks. The build-up of Si–O–Si networks cannot be controlled and the uniform coating of the filler surface becomes more difficult resulting in thicker, uncoordinated layers. These observations of the silanes hydrolysis toward pH conditions are also reported by other researchers (Kang *et al.*, 1990; Wu *et al.*, 2000; Miller & Berg, 2003; Xu *et al.*, 2010)

Complete hydrolysis of functional trialkoxysilane takes place within a period of few minutes to hours, depending on the nature of the functional group (Weissenbach & Mack, 2005). The following substituents order also gives the reactivity towards hydrolysis: alkyl $<$ vinyl \approx methacryloxy $<$ mercapto $<$ epoxy $<$ amino (Weissenbach & Mack, 2005). The following Table 2.3 shows the commercial silane coupling agent available in industry.

Table 2.3: Commercially available silane coupling agent (Tesoro & Wu, 1992).

Organofunctional group	Chemical structure	Abbreviation
Vinyl	$\text{CH}_2=\text{CHSi}(\text{OCH}_3)_3$	VS
Chloropropyl	$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	—
Epoxy		γ -GPS
Methacrylate		γ -MPS
Primary amine	$\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$	γ -APS
Diamine	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	—
Methyl	$\text{CH}_3\text{Si}(\text{OCH}_3)_3$	MS
Cationic styryl	$\text{CH}_2=\text{CHC}_6\text{H}_4\text{CH}_2\text{NH}_2^+(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3\text{Cl}^-$	—
Phenyl	$\text{C}_6\text{H}_5\text{Si}(\text{OCH}_3)_3$	—
Carboxy		—
Mercapto	$\text{HSCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$	—

Witucki (1993) reported that typically six hours are given to allow for hydrolysis and silanol or polysiloxane formation. The concentration of water, the concentration of silane, catalyst and temperature also affect the reaction rate of hydrolysis (Tesoro & Wu, 1992). Xie *et al.* (2010) stated that the number of alkoxy groups will determine the amount of water used to fully hydrolyse them and influence the adhesion between silanes and filler. To fully hydrolyse one mole of trialkoxysilane, at least three moles of water are needed. Di- and tri-alkoxy silanes produce stronger adhesion strength than mono-alkoxy silanes since they form more binding sites after they are hydrolysed.

Hydrolysis rate of silanes are also influenced by the length of the alkyl spacer that is the non-polar chain between the silane organofunctionality and the silicon atom (Xie *et al.*, 2010; Weissenbach & Mack, 2005). An α -methacryloxymethyltrimethoxy silane coupling agent with shorter alkyl chain (MMS, α -silane) can hydrolyses 20 times faster than a γ -methacryloxypropyltrimethoxy silane (MPS, γ -silane) (Figure 2.15) in an acetone/water mixture at pH 4 (Miller & Berg, 2003). This is due to the stronger electron interaction between the functionality (X) and the silicon atom (Xie *et al.*, 2010) or the lower solubility of the non-polar silanes in the aqueous reaction system (Weissenbach & Mack, 2005).

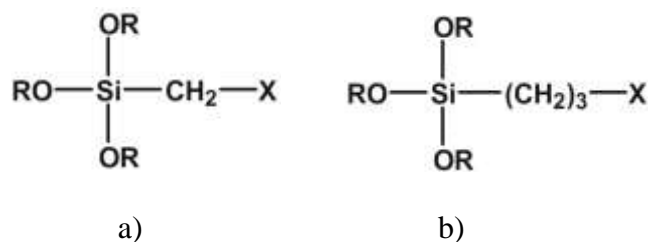


Figure 2.15: a) α -methacryloxymethyltrimethoxy silane and
b) γ -methacryloxypropyltrimethoxy silane (MPS, γ -silane)

2.3.3 Maleic anhydride coupling agents

Maleated polypropylene (MAPP) or maleated polyethylene (MAPE) has been well established as compatibilizers for wood – PP or wood – PE composites (Renner *et al.*, 2010; Clemons, 2010; Chowdhury & Wolcott, 2007; Ghaemy & Roohina, 2003; Sanadi *et al.*, 1994; Sapiha *et al.*, 1990; Myers *et al.*, 1991, Maldas & Kokta, 1991). The following Figure 2.16 shows the mechanism's steps involved in grafting of maleic anhydride to the polyethylene to produce MA-g-PE. This process was done in the presence of a peroxide radical initiator to promote reactions. This process is normally used in WPC to help improving the parent polymers physicochemical properties and to promote adhesion or crosslinking with the plastic matrix and chemical covalent bonding and polar interaction with the wood materials. Esterification will occur through the reaction of anhydride and the hydroxyl group of the wood material. The reaction mechanism of the MAPP coupling agent in WPC is as shown in Figure 2.17.

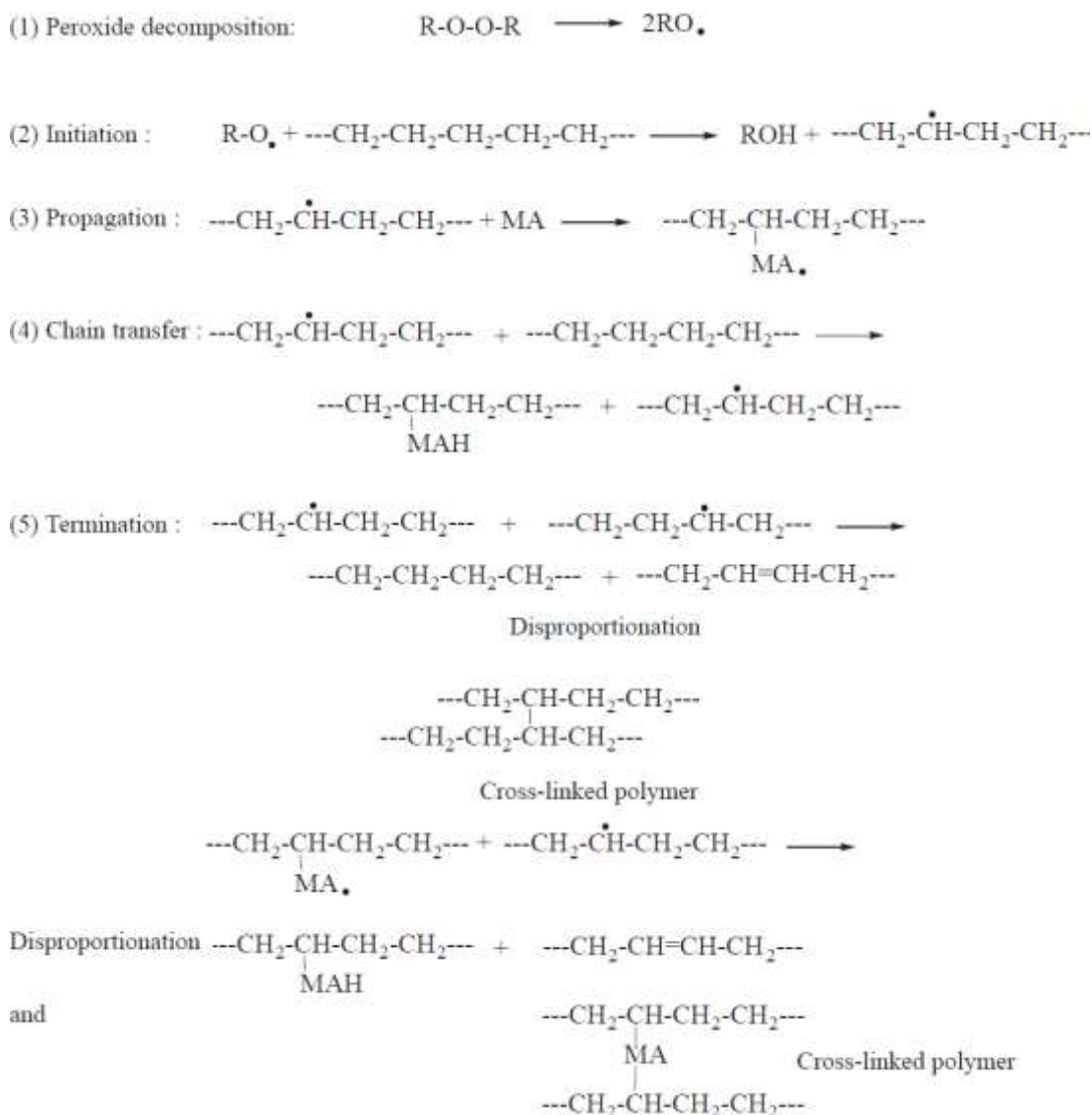


Figure 2.16: Grafting of maleic anhydride to polypropylene (Ghaemy & Roohina, 2003).

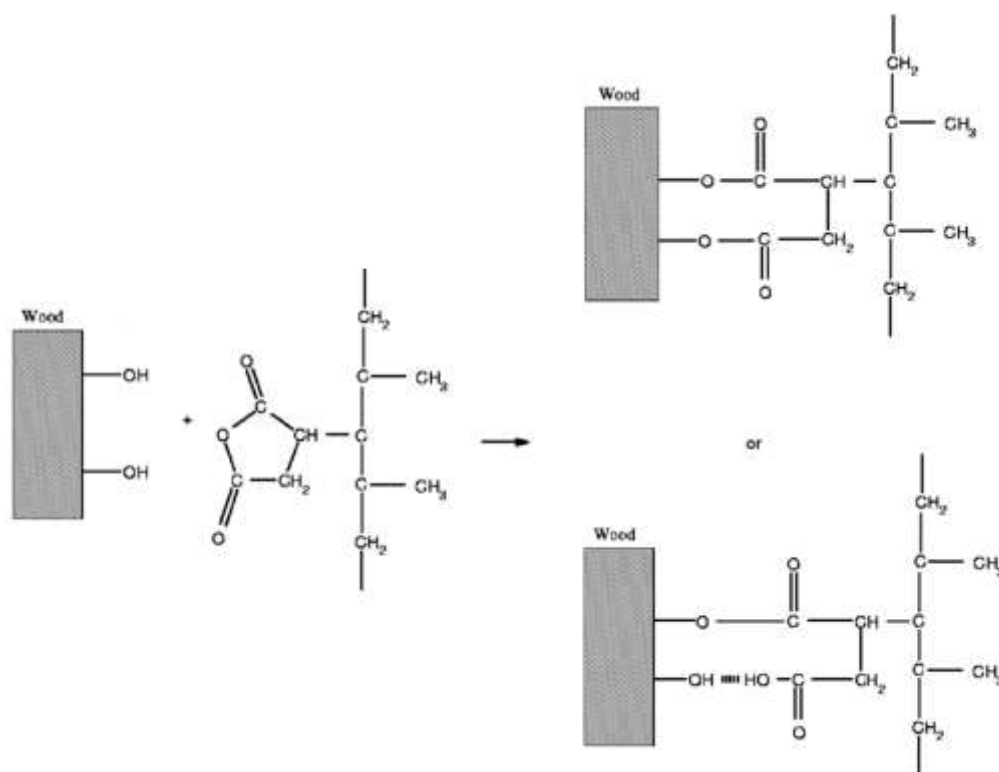


Figure 2.17: Esterification of cellulose by MAPP (Bledzki *et al.*, 1996).

2.3.4 Isocyanates coupling agents

Isocyanates ($-N=C=O$) have been used as adhesive for wood based panels for more than 25 years. Their main application is the production of exterior-grade waterproof panels and also the production of panels from raw materials that are difficult to glue like straw, bagasse, rice shells or sugar cane bagasse (Pizzi, 2005a). The functional NCO – group is potentially reactive with the hydroxyl group from the lignocellulose, making it suitable as a coupling agent in WPC system. The most common polyisocyanates are based on aromatic isocyanates, toluene diisocyanates (TDI) and methylene diphenyl diisocyanates (MDI). Aliphatic isocyanates include those based on hexamethylene diisocyanates and isophorone diisocyanates. Polyisocyanates that have been used in WPC are normally such as 4,4-diphenylmethane diisocyanate (MDI), Toluene-2-4-diisocyanate (TDI) or 1,6-diisocyanatohexane (DIC) 1-6 hexamethylene diisocyanate (HMDIC) and so on (Gironès *et al.*, 2007; Zhang *et al.*, 2006; Qiu *et al.*, 2005).

Normally the reaction of isocyanates group with hydroxyl group leads to the formation of urethane bridges which will finally give to a hardened, crosslink network:



This theory has been used in coupling isocyanates with cellulose hydroxyl group to form covalent bonding.

Karmarkar *et al.* (2007) have proven that bridge of *m*-isopropenyl- α,α -dimethylbenzyl-isocyanate (*m*-TMI) has occurred between polypropylene and wood when they grafted the *m*-TMI to the polypropylene and compounded the mixture with wood. The grafting process was done in a twin screw extruder using DCP as a radical initiator. The coupling reaction was reported to improve the mechanical properties of the composites such as tensile and flexural strength. However, as usual the addition of wood fibre to the plastic polymer decreases the impact strength and elongation at break. The following reaction was proposed to occur in the composite system.

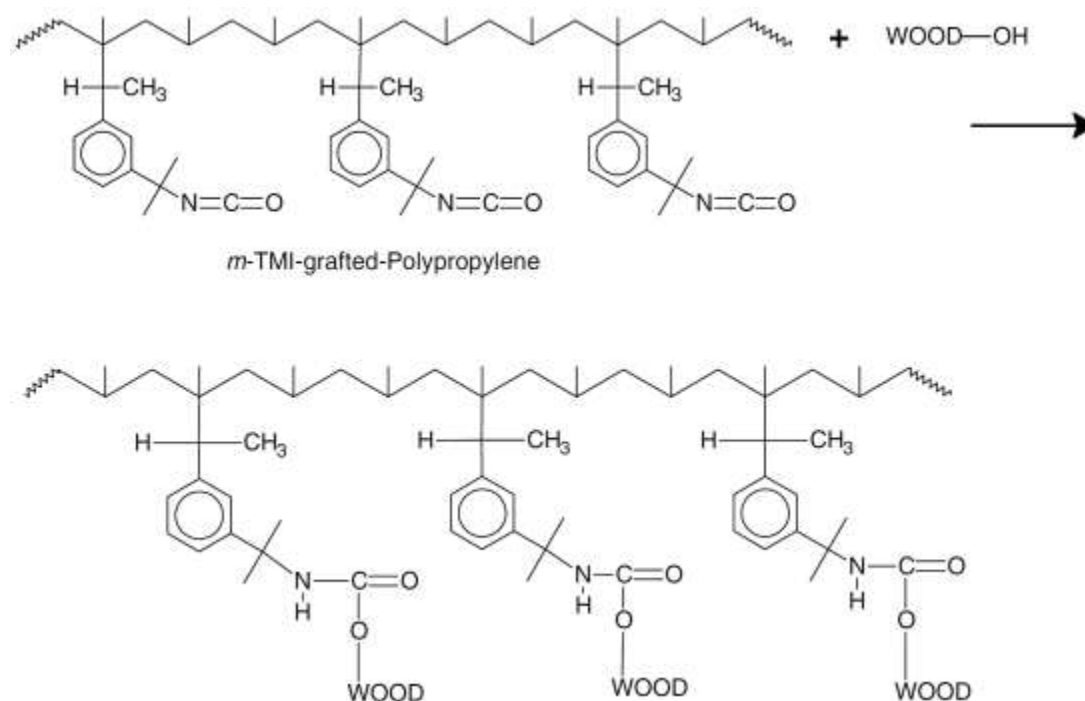
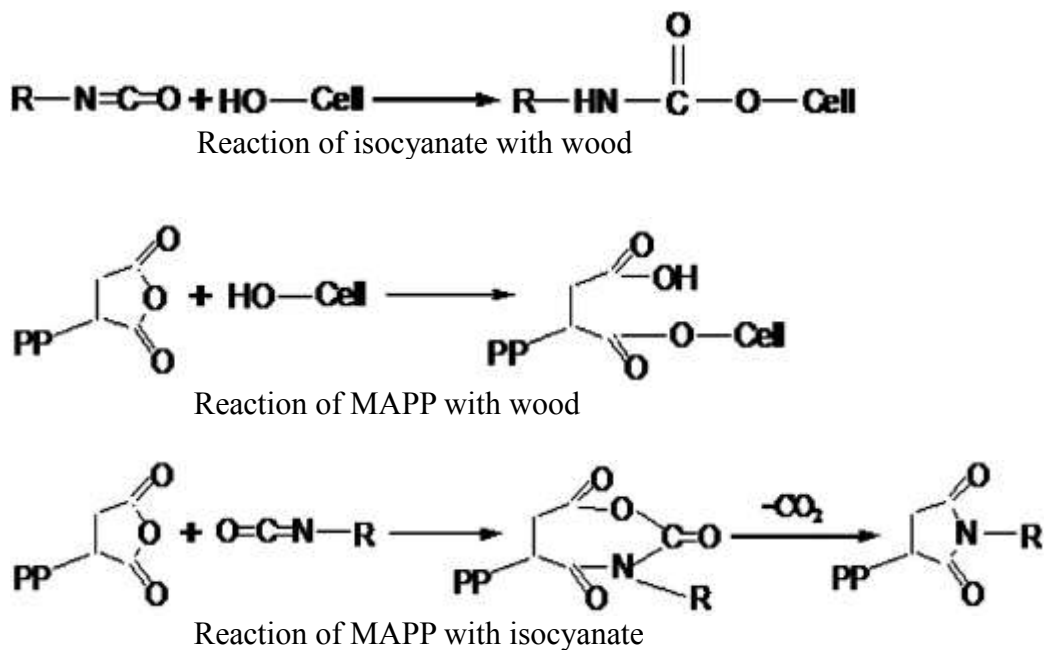
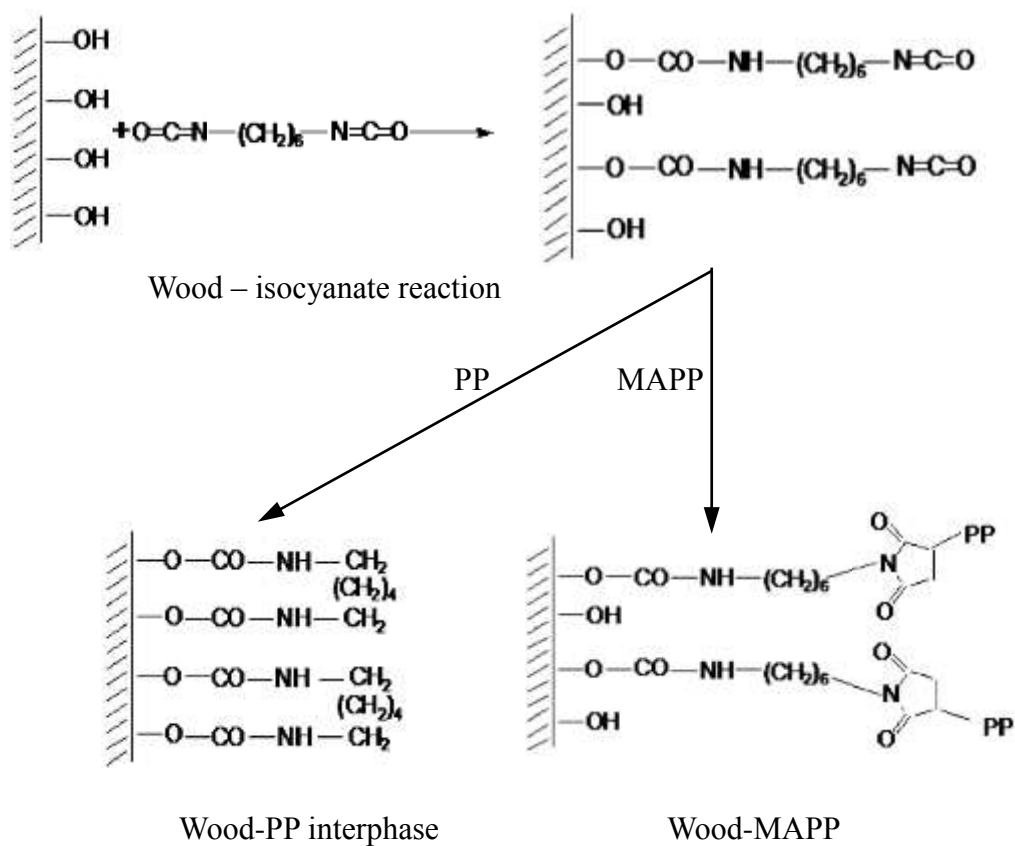


Figure 2.18: Coupling reaction of *m*-TMI grafted PP with wood fibre (Karmarkar *et al.*, 2007).

In another study reported by Qiu *et al.* (2005), it was suggested that isocyanates specifically 1,6-diisocyanatohexane may be used as a compatibilizing agent for PP/cellulose composite as well as MAPP/cellulose composite. The composites obtained were more hydrophobic, thus increasing the compatibility of PP-wood matrices and improving the mechanical properties. The following reaction model was proposed to occur in their system.

**Figure 2.19:** Bonding reaction of isocyanate, MAPP and wood**Figure 2.20:** Coupling reaction of isocyanate between wood and PP or MAPP

2.3.5 Polydimethylsiloxane Coupling Agents

Polydimethylsiloxane (PDMS) ($-(\text{CH}_3)_2\text{SiO})_n-$) or occasionally called dimethicone is the most commonly known organosilicon based polymer (Parbhoo *et al.*, 2002). PDMS is optically clear and in general, is considered to be inert, non-toxic and non-flammable. This unique type of polymer consists of an organic and inorganic part. The inorganic part constructs the backbone of alternating silicon and oxygen atoms (Figure 2.21). This Si-O bond known as siloxane bond confers to the polymer name polysiloxane. There are a variety of polysiloxane structures that can be synthesized, from simple linear to highly complex three-dimensional structures, which can be further functionalized and designed for specific applications.

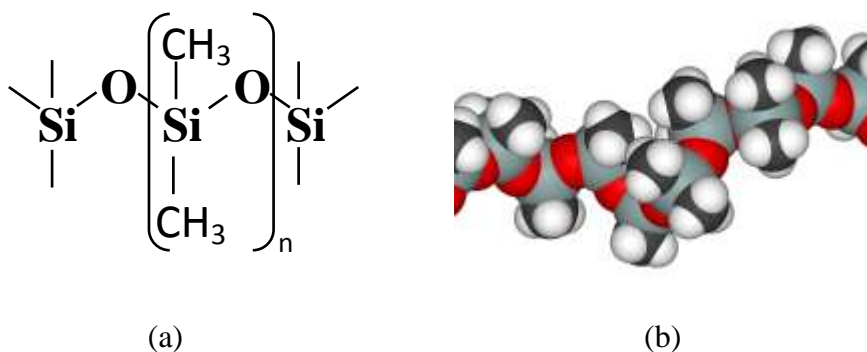


Figure 2.21: (a) Polydimethylsiloxane structures (b) A three-dimensional model of polydimethylsiloxane (Kallio, 2005)

Polysiloxane possesses a large range of properties including low surface energy, hydrophobicity, chemical resistance, electrical insulation, resistance to weathering, stability to extremes temperature, resistance to thermal shock, high elasticity, good tear strengths, capability to seal or bond materials of various natures, biocompatibility and etc. (Parbhoo *et al.*, 2002). Another unique feature of this material is the possibility in modifying the molecular structure of polymers and composing formulations that will provide specific adhesion properties leading to the development of products such as the adhesives, sealants and coupling agents, where adhesion ranges from very low to very high strength (Parbhoo *et al.*, 2002). Polysiloxanes are also an important class of polymers that have many applications in the area such as cosmetic and personal care products, foods, detergents, polishes and medicines (Fendinger, 2000).

PDMSs are very unique with their flexibility, low surface tension and other characteristics as described by Parbhoo *et al.*, 2002 as listed:

- PDMSs have very flexible nature of the inorganic backbone where the energy required to rotate around bonds is practically zero. This allows the minimum energy configuration to be easily attained.

- They have a very low intermolecular force and large Si-O-Si bond angle (149° at equilibrium) giving the ability to the methyl groups to closely pack at the surface.
- They have excellent low adhesion that is at the origin of release behaviour, which prevents most materials from strongly adhering to them but conversely, their low surface tension allows them to wet almost all surfaces.
- They have low glass transition temperatures (T_g -125 °C) due to the flexibility of the siloxane backbone and its large free volume and mobility.
- The polymer also exhibits crystallization behaviour and displays a melting transition temperature (T , -40 °C) that is dependent on the rate of cooling.
- The large free volume and mobility of polysiloxanes give rise to a high diffusion coefficient and high permeability of gases or vapours. Oxygen, for example, diffuses through PDMS much more quickly than through other polymers. Water vapour that has a low solubility value also passes through PDMS very quickly due to its high diffusion coefficient.

The simplest forms of PDMS are straight chain polymers carrying no special substituents and are generally sold according to viscosity or molecular weight (De Poortere, 2005). Their chain length can vary to ten thousands giving a range of viscosity from 0.65 to 2 500 000 centipoises. This allows the use of PDMS in the form from water like fluid to flowable gum (Parbhoo *et al.*, 2002). Specific properties can be conferred on PDMS by substitution with functional groups. Groups such as alkoxy, amino and mercapto will mainly interact with substrates by hydrogen bonding. Others such as unsaturated or epoxy groups can cross-link by covalent bond formation (De Poortere, 2005).

PDMSs have been widely used in other fields such as coating technology (Esteves *et al.*, 2010; Fang *et al.*, 2010), membrane separation technology (Ulbricht, 2006; Li *et al.*, 2010), nanocomposites (Chakrabarty, 2010; Ma *et al.*, 2010) and in rubber technology (Mani *et al.*, 2010; Maxwell, 2009) and they work well to form cross linking in the coating system and rubber technology and separate selectively in membrane technology but to the best of our knowledge, the use of PDMS as a coupling agent in the wood flour/PP system has not yet been reported.

Research on silicone materials as a coupling agent arose in the 1940s when glass fibres were first used as reinforcement in unsaturated polyester (UP) resin. However, it was silane and not polysiloxane appeared to be discovered earlier to couple the composites' component and enhanced the properties (Weissenbach & Mack, 2005). Since then, a lot of researches and developments of silane as the coupling agent has been made and reported in various composite systems (Bengtsson & Oksman, 2006; Bengtsson *et al.*, 2006; Ichazo *et al.*, 2001; Pickering *et al.*, 2003; Hu *et al.*, 2006). Chemical modification of fillers with silanes may generate the following performance benefits as listed by Weissenbach and Mack (2005) and Edser (2003):

- Improved dimensional stability
- Modified surface characteristics (water repellency or hydrophobicity)

- Improved wet-out between resin and filler
- Decreased water-vapour transmission
- Controlled rheological properties (higher loadings with no viscosity increase)
- Improved filler dispersion (no filler agglomerates)
- Improved mechanical properties and high retention under adverse conditions
- Improved electrical properties

Silane coupling agents have been used in WPC for years and as been shown previously in Table 2.3, there are various types of commercially available silane coupling agent in the market. However, without having to go through the hydrolysis and condensation steps which could be influenced by various factors and conditions during a reaction, as explained in section 2.3.2, polysiloxane will offer a better choice. More choices of functional groups could attach to them to give differences in coupling reaction. Polysiloxane will also offer a more specific structure and molecular weight information before coupling reaction takes place, which will help in predicting or controlling the end product.

2.4 Theoretical Basis of Adhesion

In a composite system, bonding at an interface normally is due to adhesion between filler and matrix. As has been explained in the previous literature review, (the whole section 2.3) the adhesion between wood and plastic occurs at both wood and plastic interfaces when a coupling agent is used. As shown in the reaction mechanisms, the coupling agent normally will react with the free hydroxyl groups on the wood surface at one end and the other end will bond with the plastic matrix. This coupling reaction will bridge both wood and plastic surface together and is known as an interphase in three-dimensional (Figure 2.22). It is the ability in sticking together two surfaces so that stress can be transmitted between them. It can be quantified by the amount of work which is required to pull two surfaces apart (Niska & Sanadi, 2008). The effect of the interphase on the properties of a composite material depends on its amount and characteristics. It plays a very important role in determining properties such as strength, toughness and long term properties such as creep and moisture stability. Poor adhesion between filler and matrix in a composite system decreases the adhesion between them. The following Figure 2.22 shows a schematic of the adhesion mechanisms.

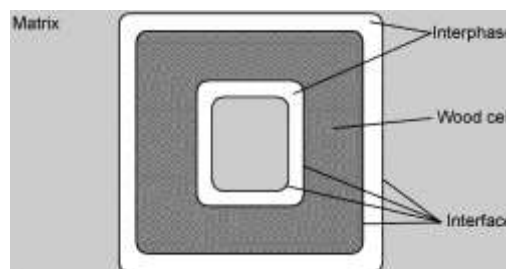


Figure 2.22: A schematic description of an interface and interphase in a cross-section of WPC (Niska & Sanadi, 2008)

There exist two interfaces, as mentioned earlier. One is between the matrix and the interphase and the other one is between the interphase and the wood. So theoretically when a load is applied to the composite, several failure scenarios can occur. Generally, because various factors are to be taken into accounts, these failures are very complex to be discussed. However, we can classify them into two categories: adhesive failure and cohesive failure. Adhesive failures occur at the interfaces and the cohesive failure occurs at the interphase. The following Figure 2.23 shows the failure modes in WPC as illustrated by Niska and Sanadi (2008).

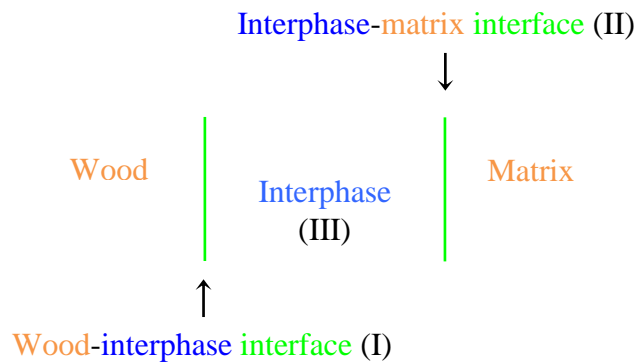


Figure 2.23: Schematic of three distinct failure modes; adhesive failure (I and II) and cohesive failure (III)

Table 2.4: Bond types and typical bond energy (Pizzi, 1994)

Type	Bond energy (kJ/mol ⁻¹)
Primary bonds	
Ionic	600 – 1100
Covalent	60 – 700
Metallic, coordination	110 – 350
Donor-acceptor bonds	
Bronsted acid-base interactions (Up to a primary ionic bond)	Up to 1000
Lewis acid-base interactions	Up to 80
Secondary bonds	
Hydrogen bonds (excluding fluorine)	1 – 25
van der Waals bonds	
Permanent dipole-dipole interactions	4 – 20
Dipole-induced dipole interactions	Less than 2
Dispersion (London) forces	0.08 – 40

Theoretically there are five main mechanisms of adhesion that can occur at the interface either in isolation or in combination to produce the bond. They are:

- adsorption and wetting,
- interdiffusion,
- electrostatic attraction,
- chemical bonding,
- mechanical interlocking

(Hull, 1995).

Various types of bond can occur through these mechanisms, which can be grouped as primary bond, donor-acceptor bond and secondary bond as listed in Table 2.4.

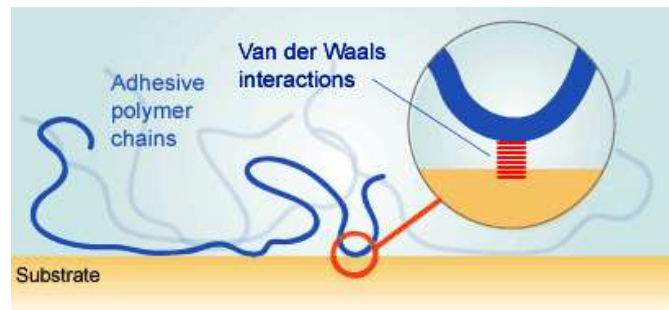


Figure 2.24: Bond formed by adsorption (illustration from SpecialChem)

(i) *Adsorption and wetting* mechanism occur when two electrically neutral surfaces are brought sufficiently close together where a physical attraction takes place (Hull, 1995). Normally interatomic and intermolecular forces between the atoms and molecules of the two materials will take place (Parbhoo *et al.*, 2002). In the case of wood adhesion normally the secondary forces that are including the van der Waals forces, hydrogen bonds and electrostatic interactions appeared to play the dominant role (Pizzi, 1994). They are of great importance in achieving good adhesive interactions between the two phases. If we take wood flour/PP surfaces as an example, the adhesion is characterized by the degree of direct interfacial contact between wood flour and PP polymer surfaces which is also called as wetting.

Wetting could be discussed further using contact angle and surface tension of liquid drop on a solid surface theory (a short discussion is given in appendix 2, appendixes section). Wetting can be improved by changing the surface energetics of the system such as increasing the filler surface energy and/or lowering the polymer surface energy. This can be achieved using suitable surface treatments or by addition of interfacial active additives. PDMS based polysiloxane polymers appear to have a very low liquid-vapour surface tension (γ_{LV}) (~22 mN/m), which is lower than the critical surface tension (γ_C) of most substrates. Therefore, they could wet and spread

easily on most surfaces and they have been widely used in the adhesion science technology (Parbhoo *et al.*, 2002). This thermodynamically driven property ensures that surface irregularities and pores are filled with adhesive, giving an interfacial phase that is continuous and without voids. The gas permeability of the silicone will allow any gases trapped at the interface to be displaced. Thus, maximum van der Waals and London dispersion intermolecular interactions are obtained at the silicone-substrate interface (Parbhoo *et al.*, 2002). The γ_C of softwood listed by Piao *et al.* (2010) is between 42.5 to 53.2 mN/m. Thus PDMS was predicted to adhere to wood flour/PP composite effectively.

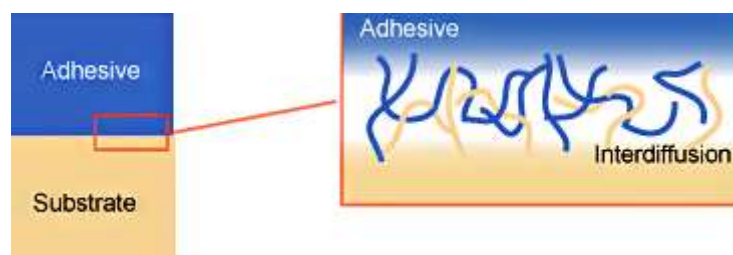


Figure 2.25: Bond formed by molecular entanglement following interdiffusion (illustration from SpecialChem)

(ii) *Diffusion* theory involves the interdiffusion of macromolecules across the interface (Figure 2.25). The original interface becomes an interphase composed of mixtures of two polymer materials entirely due to molecular entanglement (Parbhoo *et al.*, 2002). This theory suggests that the macromolecules of both the adhesive and the substrate, or chain segment of them, possess sufficient mobility and are mutually soluble (Pizzi, 1994).

Pizzi (1994) explained this effect using the concept of solubility. The requirement can be expressed by the condition that the polymers of the adhesive and those of the substrate possess similar solubility parameter values, this being a rating of the compatibility of the two materials. The polymer needs to be amorphous; as a high degree of crystallinity tends more to resist dissolving in the solvent (the concept of the solubility parameters does not take crystallinity into account). Hull (1995) also stated that interdiffusion may be promoted by the presence of solvents and plasticizing agents, and the amount of diffusion will depend on the molecular conformation and constituents involved and the ease of molecular motion.

Wood is not a homogeneous substrate. It is primarily a cellular composite of three polymers: cellulose, mostly crystalline but also amorphous, and hemicellulose and lignin, which are both amorphous. On the other hand, PP is a semi crystalline polymer. It is clear from the solubility parameter concept that some polymers, the amorphous ones, such as hemicellulose and lignin, and the amorphous portion of cellulose or PP could undergo mutual diffusion (Pizzi, 1994). The crystalline portion of cellulose or the PP is not likely to be involved.

The level of interaction and adhesive depends on the amount of molecular entanglements and the number of molecules involved. It is reported by Oksman *et al.* (1998) that coupling agent such as MAPE results in chemical bonding between the anhydride moiety and the wood fibre surface, while interdiffusion occurred on the other end of MAPE with the matrix. Molecular weight of adhesive or coupling agent is also important to be considered because a minimum chain length is necessary to obtain optimized stress transfer and adhesive strength (Niska & Sanadi, 2008). PDMS consists of a very flexible Si-O-Si backbone and various selections of chain length and molecular weight could be chosen depending on our need. So theoretically when PDMS with suitable chain length and molecular weight has been chosen, interdiffusion mechanism might occur in our composite system.

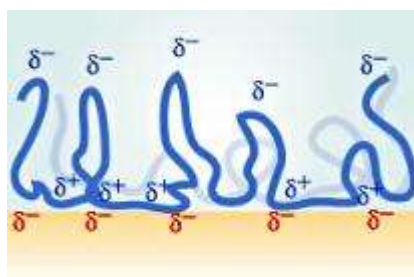


Figure 2.26: Bond formed by electrostatic attraction where cationic groups at the end of molecules attracted to an anionic surface resulting in polymer orientation at the surface (illustration from SpecialChem)

(iii) *Electrostatic attraction* occurs between two surfaces when both surfaces carrying different charge come close together (Figure 2.26) and normally occurs in the case of acid-base interaction and ionic bonding. When a coupling agent containing ionic functional group is used, it is expected that cationic functional groups will be attracted to an anionic surface and vice versa. By controlling the pH, these coupling agent molecules can be oriented on the substrate surface to get a maximum coupling effect. Some chemical bonding normally will also be involved in this mechanism. The strength of the interface will depend on the charge density (Hull, 1995; Niska & Sanadi, 2008). A lot of works have reported that by controlling the pH of silane solution to slow down condensation during hydrolysis, more reactive silanol will access the wood hydroxyl group or glass fibres and perform covalent bonding. An acidic pH environment is usually preferable to accelerate the hydrolysis rate, but slow down the condensation rate of silanols (Xie *et al.*, 2010; Navoroj *et al.*, 1984; Gwon *et al.*, 2010; Weissenbach & Mack, 2005).

(iv) *Chemical bonding* is formed between chemical grouping on the filler surface and the compatible chemical group in the matrix (Figure 2.27). Normally strong covalent bonding occurs. The strength of adhesion depends of the number and the type of bonds. It is also possible to enhance the chemical bonding through the use of adhesion promoters or coupling agent and chemical modification of the substrate surface (Hull, 1995; Niska & Sanadi, 2008; Parbhoo *et al.*, 2002).

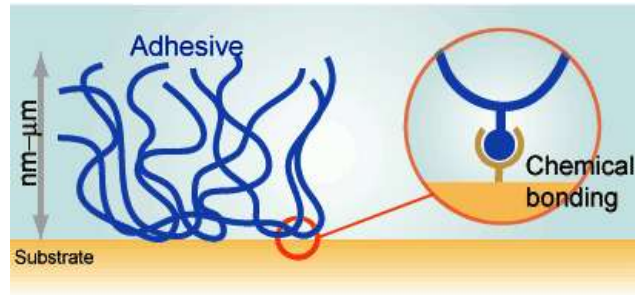


Figure 2.27: Chemical bonding formed between substrate chemical groups and adhesive chemical group on the other surface (illustration from SpecialChem)

Bengtsson and Oksman (2006) have reported that chemical bridging between the matrix and the fibre surface has occurred when they used silanes as the coupling agent in their WPC system. They claimed that siloxane bridges were formed on the fibre surface and silane-polymer interaction on the other end. As reported earlier, Oksman *et al.* (1998) has also stated the formation of chemical bonds on the fibre surface when they used Maleated polyolefins while the other end of the anhydride grafted polymer molecules physically entangled with the polymer matrix.

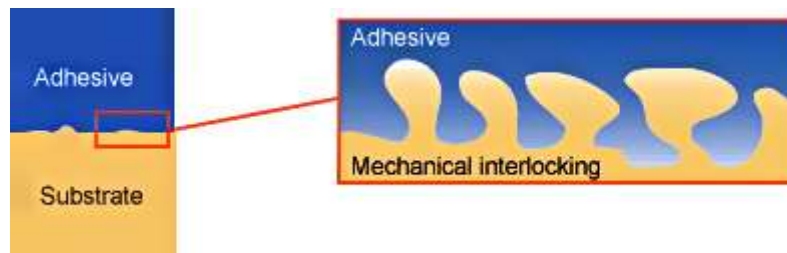


Figure 2.28: Mechanical interlocking formed when a liquid polymer wets a rough solid surface (illustration from SpecialChem)

(v) *Mechanical interlocking* occurs when a resin that completely wet the filler surface follows every detail of that surface (Figure 2.28). The work of adhesion will be increased by the surface roughness because of increased in the surface area. The tensile strength of this interface is normally low. However, it would be high if there were a large number of re-entrant angles on the filler surface. Nevertheless, the shear strength may be very significant and depends on the degree of roughness (Hull, 1995; Niska & Sanadi, 2008).

2.5 Interphase Characterization and Dynamic Mechanical Analysis

Dynamic Mechanical Analysis (DMA) measures the mechanical properties of materials as a function of time, temperature, and frequency. An oscillating force will be applied to deform a specimen. Then, the material's response to that force will be analysed. The tendency of material to flow (viscosity), the stiffness (modulus) from

the sample recovery and the ability to lose energy as heat (damping) can be calculated. The terms loss modulus (E'') is used to describe the dissipated energy as heat during measurement and the stiffness or storage modulus (E') is to describe the elastic response. In other words, E' related to the ability of material to return energy and the E'' to lose energy when forces are applied. The ratio of storage and loss modulus gives the tan delta, a mechanical damping or internal friction that indicates the material elasticity. A high tan delta value indicates that the material has high non-elastic strain component while a low value indicates that the material is more elastic. This relationship of E' and E'' has been schematically described by Menard (2008) as a bouncing ball (Figure 2.29). The larger E' is relative to E'' , the more of the energy required to deform the specimen is elastically recoverable. The larger E'' is relative to E' , the more of the deformation energy is viscously dissipated as heat (Menard, 2008)

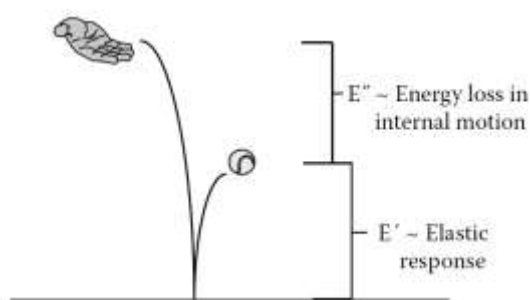


Figure 2.29: A bouncing ball describing storage modulus E' (the recovered part that is how high it bounced) and loss modulus E'' (the difference between the height dropped from and the bounce) (Menard, 2008).

DMA measurements can be used to describe the relaxation of the polymer chain in a specimen which shows the transition state material passes through when heated (Figure 2.30), in the matter of time or frequency. It also can describe the change in the free volume that occurs in the polymer (Figure 2.31). Free volume is defined as the space a molecule has for internal movement (Menard, 2008). Both polymer relaxation and free volume descriptions will give the information on the changes in the sample at the molecular level which is closely related to bonding and adhesion in the sample.

From Figure 2.30 we can see several transitions of an idealized polymer respond when heated. As explained by Menard (2008), at a very low temperature the polymer is in solid-state transition and the molecule is tightly compressed. When heated, the polymer chain will start to expand and increases the free volume thus movements of the side chain and localized bond (bending and stretching) can occur. This is known as gamma transition (T_γ) and may also involve association with water. Beta transition (T_β) occurs as the temperature and free volume continue to increase where the whole side chains and localized group of four to eight backbone atoms begin to have enough space to move and the material starts to develop some toughness. This transition also sometimes is the glass transition (T_g) of a secondary component in a blend or of a specific block in a block copolymer. T_g will occur as

heating continues and it only occurs in amorphous regions when the chains in these regions begin to coordinate large-scale motions. This transition is normally seen as a sudden drop of the storage modulus. Polymer blends or composites with good interfacial adhesion normally will show a higher T_g due to the more difficult movements of the polymer chain. T_a^* is the transition when slippage of crystallites occurs in crystalline or semi crystalline polymer and T_H is a movement of coordinated segments in the amorphous phase that relates to reduced viscosity. The melting temperature (T_m) is finally reached when the large-scale chain slippage occurs and material flows as heating continue.

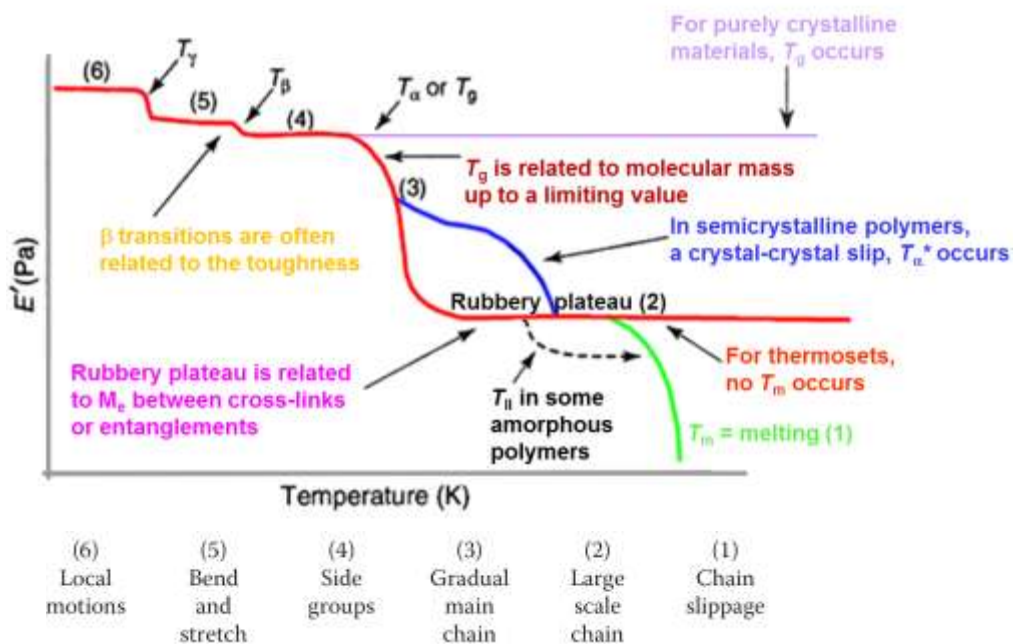


Figure 2.30: An idealized scan showing the effect of various molecular relaxations on the storage modulus curve Menard (2008)



Figure 2.31: Free volume in polymer (illustration from The glass transition)

DMA results with frequency ramp can be used to calculate the activation energy (E_a) that is the energy needed to cause a motion. It is the minimum energy required to promote a reaction between two molecules by stretching, breaking

chemical bonds or forming new bonding (Oxford, 2005) or also referring to the energy required to cause a molecule of polymer chain segment to jump from its present position to a nearby hold, which is an empty volume of a molecular or chain-segment size (Gooch, 2007). The higher the activation energy is, the better the interaction, bonding or adhesion within the polymer chains or molecules is. The activation energy is calculated from the glass transition relaxation temperature using the rearrangement of Arrhenius equation as has been shown below:

$$f = f_o^{-E_a/RT} \quad \text{Equation 2.1: Arrhenius Equation}$$

$$\ln f = \ln f_o - E_a/RT$$

$$\ln f = - \frac{E_a}{R} \left[\frac{1}{T} \right] + \ln f_o \quad \text{Equation 2.2: Rearrangement}$$

where;

f = rate constant / test frequency

f_o = frequency factor

E_a = activation energy

R = ideal gas constant (8.314 J/(mol K))

T = temperature (K)

From Equation 2.2, E_a can be calculated by figuring out the maximum temperatures of the tan delta at the different frequency and depicting the Arrhenius-plot of the composites, which is a straight line of $\ln f$ versus $1/T$ (Gabbot, 2008). The E_a can be calculated from the slope of the plot multiplied to the gas constant. Li *et al.* (2000) stated that the E_a is more reliable to be determined from the loss tangent (tan δ) peak.

2.6 Processing WPC using a twin-screw extrusion compounding

There are several ways of processing wood and plastic polymer to produce WPC. The choices are depending upon achieving a uniform distribution of well wetted-out individual particles or fibres into the polymer, either with batch or continuous equipment.

Batch mixers allow control of the sequence of addition the ingredients to obtain the final desired product without the need for multiple feeders and they are better in controlling the processing parameter (residence time, shear and temperature). However the batch mixers may be difficult in emptying and extra processing is required for the end product shaping. On the other hand, the continuous compounding systems do not have the problem of fluctuations in quality of different batches as well as difficulty in emptying or end product shaping (Optimat & Merl, 2003; Todd, 2005).

For most applications in processing composites, extruders, either single-screw or twin-screw, normally become the first choice to achieve the desired compounds. This is because of the various tasks being able to be accomplished in extrusion compounding as listed by Todd (2005):

- Metering and feeding of the ingredients
- Melting of solid-fed polymers
- Break-up of agglomerates
- Providing uniform distribution of the filler
- Venting
- Developing pressure for discharge.
- Avoiding excessive screw and barrel wear
- Minimizing energy consumption.

There may be significant differences between single- and twin-screw extruders in how they achieve the above functions. However a single screw extruder normally has more disadvantages compared to a twin screw extruder such as poor mixing characteristics, lower output rate, greater risk of burning and so on (Optimat & Merl, 2003).

Twin-screw extruders (Figure 2.32) are classified as intermeshing or non-intermeshing, and co-rotating or counter-rotating with parallel or conical screw. Figure 2.33 shows the different between the conical and parallel screw.

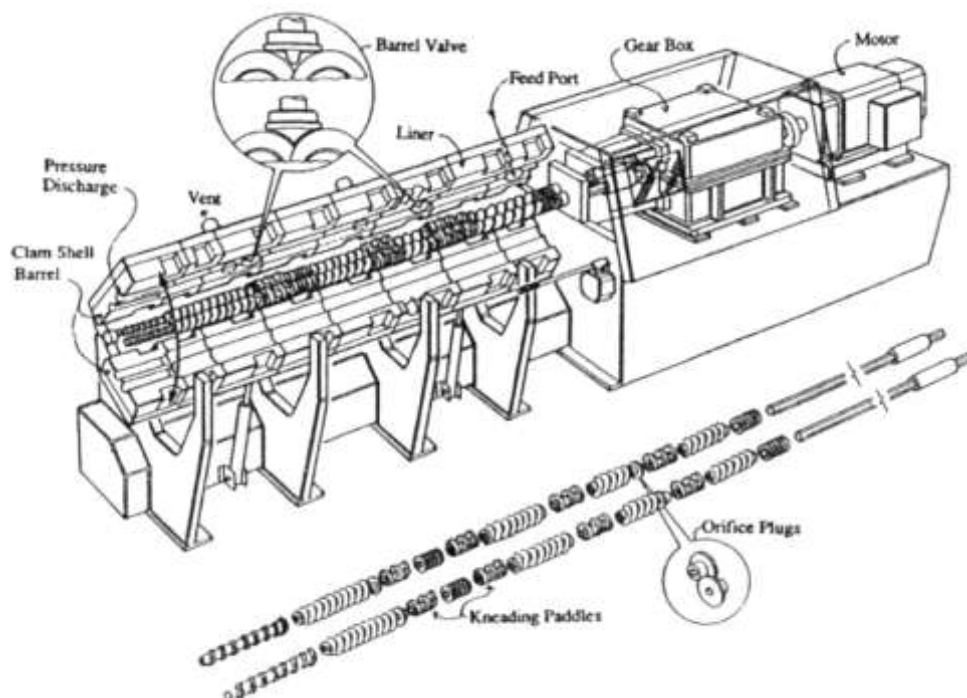


Figure 2.32: Co-rotating intermeshing twin-screw extruder (Todd, 2005).

Basically, the conical screw is suitable for material with low apparent density such as wood fibre because of larger screw diameter in the feed section and increasing compression along the screw. It also has wider processing range and can cope with different output requirements and variations in the raw material properties better than parallel machines. The screws' slimness in the metering section means that the shear stress on the material is minimized. This has a particular advantage of keeping the wood fibre intact.

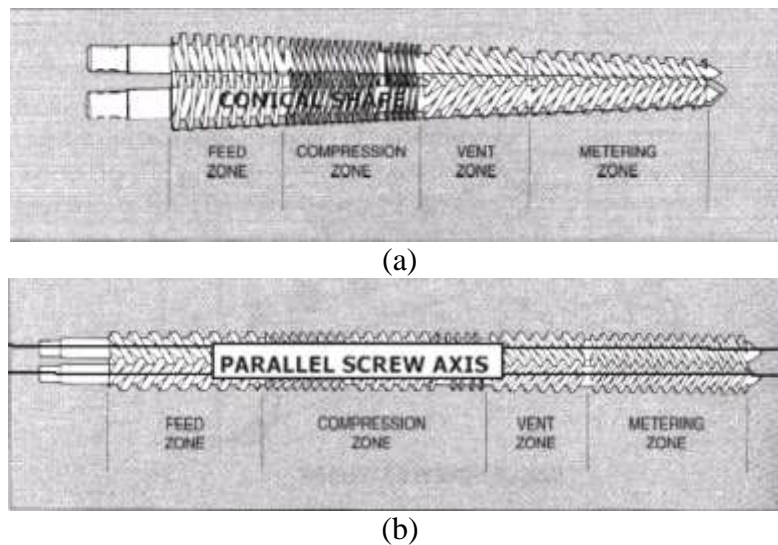


Figure 2.33: The different between (a) conical and (b) parallel twin-screw extruder (Optimat & Merl, 2003)

Table 2.5: Classification of twin-screw extruder (Todd, 2005)

SCREW ENGAGEMENT		SYSTEM	COUNTER-ROTATING	CO-ROTATING
INTERMESHING	FULLY INTERMESHING	LENGTHWISE AND CROSSWISE CLOSED		THEORETICALLY NOT POSSIBLE
		LENGTHWISE OPEN AND CROSSWISE CLOSED	THEORETICALLY NOT POSSIBLE	
		LENGTHWISE AND CROSSWISE OPEN	THEORETICALLY POSSIBLE BUT PRACTICALLY NOT REALIZED	
	PARTIALLY INTERMESHING	LENGTHWISE OPEN AND CROSSWISE CLOSED		THEORETICALLY NOT POSSIBLE
		LENGTHWISE AND CROSSWISE OPEN		
NOT INTERMESHING	NOT INTERMESHING	LENGTHWISE AND CROSSWISE OPEN		

Table 2.5 shows the classification of co-rotating and counter-rotating twin-screw extruder. Normally, the counter-rotating is used for production of very high dispersion compounds because materials will be forced through the screw at very high pressure, which is unsuitable for fibre compounding. Further comparisons are shown in Table 2.6.

Table 2.6: Comparison between co-rotating and counter-rotating Twin-Screw Extruders (Bash & Karian, 2003)

	Corotating	Counterrotating
	<i>L/D</i> ratio up to 60:1, screw speed up to 1400 rpm	<i>L/D</i> ratio usually < 24:1, screw speed usually < 150 rpm
Distributive mixing	Good to excellent This is due to high degree of radial mixing between pairs of intermeshing elements with material transport from one shaft to the other at a given axial location	Poor
Dispersive mixing	Good	Excellent The movement of material between the calender gap of the two screws is similar to Banbury-type mixing
Flow in longitudinal direction	Open system	Closed system
Material conveying mechanism	Viscous drag at barrel surface	Positive displacement
Flow stability (surging)	Fair	Excellent
Pressure generation	Moderate	High
Venting capability	Fair to good	Fair
Feeding capability	Good	Good
Molten flow pattern in 8-figure cross-section	Flow around two screws just like one oval single-screw axis	Because of restraints on closed C chambers, material is forced through calender gap between screws
Attrition of glass fibers	Lower degree of glass fiber break-up	Higher break-up of glass fibers with lower mechanical properties
Melt purge properties of TiO ₂ cleaning time characteristics	Slower with self-wiping effect—much broader residence time distribution	Rapid due to sharper residence time distribution
Length of melting region	Longer in continuous screw bushing	Shorter length
Mean residence time	Same for equal free volume	Same for equal free volume
Relative operational screw speed	High	Low
Relative throughput rate	Higher at same torque	Lower at same torque

The homogeneity of a compound could be achieved with a certain processing condition. Theoretically optimum compounding can occur when the viscosity of every component in the barrel is about the same or when the materials in the barrel are in the semi-solid state having a high viscosity. The viscosity of materials in a compounder is depending on the temperature, speed and the retention times and the optimum processing temperature will be normally close to the melting point of the materials. Too high temperature will decrease the viscosity and resulting in less effective compounding, causing agglomeration and lead to degradation while too low

temperature will not lead to melting. Processing speed also gives the same effect as temperature variants. The homogeneity is optimum at a certain processing speed. The compounding rate will increase with the increasing speed before the optimum compounding achieved. The following Figure 2.34 shows the compounding morphology.

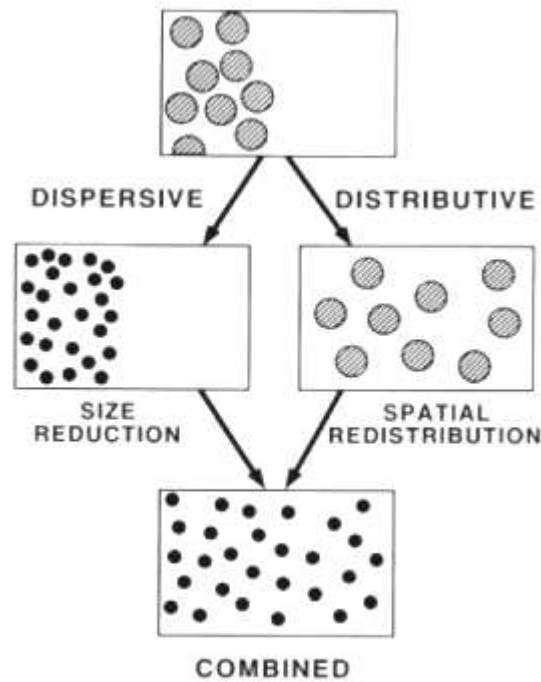


Figure 2.34: Dispersive and distributive morphology of compound.

3 Materials and Methods

3.1 Materials

All the materials used in this research, their specification, the supplier's name and how they were used are listed in Table 3.1.

3.1.1 Preparation of wood particle

Spruce wood particle sizes 0.6 mm – 1.25 mm (mid-WP) and 1.25 mm – 3.15 mm (long-WP) were prepared at the Fraunhofer Wilhelm-Klauditz-Institute (WKI), using a Condux grinder type LV 15 K, CONDUX Hanau-Wolfgang. Spruce wood were previously prepared and cut to small pieces before they were ground to small particle. After that they were sieved using Allgaier TSM 1200 sieve machine, Allgaier-Werke KG. Uhingen to get the particle sizes needed.

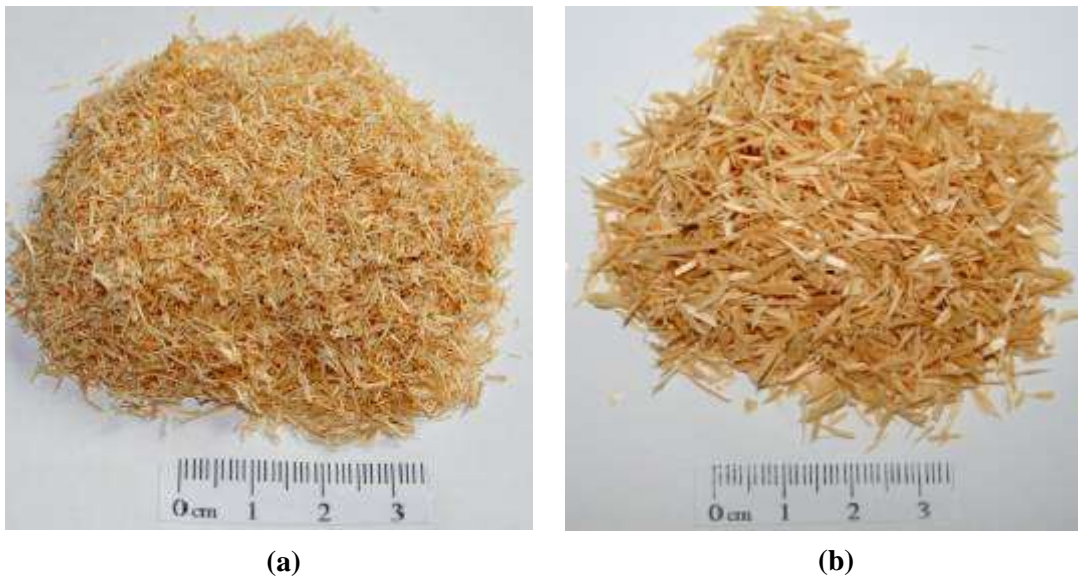
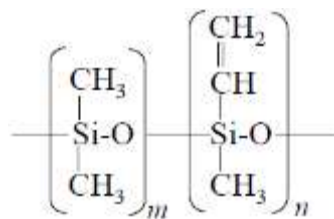


Figure 3.1: (a) Spruce wood particle sizes 0.6 mm – 1.25 mm and (b) 1.25 mm – 3.15 mm

Table 3.1: Materials and supplier

Material	Specification	Supplier	Application
Lignocel BK 40/90 wood flour (WF).	<ul style="list-style-type: none"> • Cubic structure sizes 300 μm – 500 μm from selected conifers. 	J. Rettenmaier and Söhne GmbH + Co. KG, Rosenberg, Germany	Used as received
Spruce wood particle	<ul style="list-style-type: none"> • Sizes 0.6 mm – 1.25 mm (mid-WP) and 1.25 mm – 3.15 mm (long-WP) 	WKI, Fraunhofer Institute for Wood Research, Braunschweig, Germany	Sieved using Allgaier TSM 1200 sieve machine, Allgaierwerke KG. Udingen.
Polypropylene (PP)	<ul style="list-style-type: none"> • Medium isotactic homopolymers • MFR of 10.5 g/10min and density of 905 kg/m³ 	Sabic Deutschland GmbH and Co. Gelsenkirchen, Germany.	Ground to grain size using Condux grinder type LV 15K, CONDUX Hanau-Wolfgang.
Coupling agents with 100% purity:		Evonik Goldschmidt GmbH, Essen, Germany.	Used as received in isopropanol solution
i) TEGOMER V-Si 4042 (Vinyl PDMS)	<ul style="list-style-type: none"> • Insoluble in water with density of 0.971 g/cm³ • 1 functionality ~10 000 g/mol • n to m ratio ± 1 to 133 		

Table 3.1: Materials and supplier (continued)

ii) TEGOMER VB 2706
(Triethoxy PDMS)

- Insoluble in water with density of 0.999 g/cm³
- 1 C(OEt)₃ ~ 5 000 g/mol
- *l* to *m* ratio ± 1 to 64

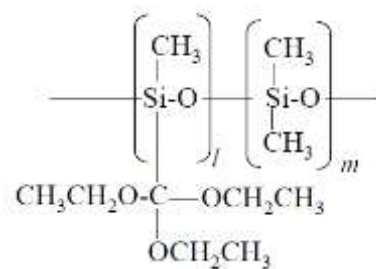


Table 3.1: Materials and supplier (continued)

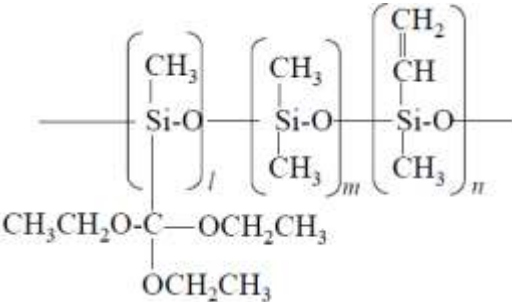
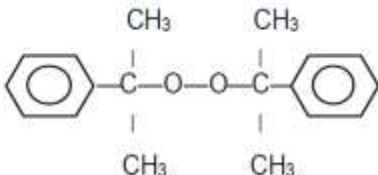
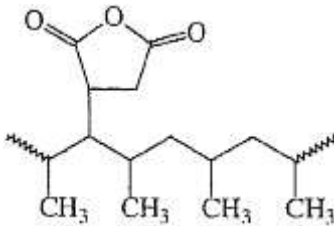
iii) Bifunctional Triethoxy-vinyl PDMS			<p>These are specially synthesized materials. Most of the information was kept confidential. Combining the little information provided, the possible structure predicted is shown with unknown ratio of l, m and n.</p>	
- TEGOMER V-Si 4042 batch VB 3242	<ul style="list-style-type: none"> • Low molecular weight • 2 500 g/mol with <100 Si units per backbone 			
- TEGOMER V-Si 4042 batch VB 3247	<ul style="list-style-type: none"> • High molecular weight • 12 000 g/mol with ± 250 Si units per backbone 			
- TEGOMER V-Si 4042 batch VB 3248	<ul style="list-style-type: none"> • Very high molecular weight • 30 000 g/mol with $\gg 250$ Si units per backbone 			
iv) Coupling agent with 50% very high molecular weight bifunctional triethoxy-vinyl PDMS:	<ul style="list-style-type: none"> • Containing the same structure as iii) with the very high molecular weight properties. 		Evonik Goldschmidt GmbH, Essen, Germany	Used as received

Table 3.1: Materials and supplier (continued)

- TEGO XP 6000 batch 294; 50% master batch VB3248 compounded in Polypropylene	<ul style="list-style-type: none"> • 50% very high molecular weight bifunctional triethoxy-vinyl PDMS compounded with PP in pellet form 	
- TEGOPREN 6875-45 batch 3248; 50% emulsion of VB 3248	<ul style="list-style-type: none"> • 50% very high molecular weight bifunctional triethoxy-vinyl PDMS in emulsion form • Density of 0.95 g/cm³ 	
v) TEGOMER H-Si 2311 (Hydroxylalkyl PDMS)	<ul style="list-style-type: none"> • Insoluble in water with density of 0.96 g/cm³ • Molecular weight is 2500 g/mol 	
<div data-bbox="757 866 1272 1074" data-label="Chemical-Block"> $\text{HO}-(\text{CH}_2)_m-\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{Si} \\ \\ \text{CH}_3 \end{array} \text{O} \begin{array}{c} \text{CH}_3 \\ \\ \text{Si} \\ \\ \text{CH}_3 \end{array} \right]_n-(\text{CH}_2)_m-\text{OH}$ <p>$n = 30$</p> </div>		
2-Isopropanol 70% pure	<ul style="list-style-type: none"> • Density of 0.87 g/cm³ • Flash point of 13 °C; Melting point of 82 °C 	Carl Roth GmbH + Co. Used as received KG, Karlsruhe, Germany.

Table 3.1: Materials and supplier (continued)

PEROXAN DC Dicumyl peroxide (DCP) 99%	<ul style="list-style-type: none"> • Crystal pellet with melting point of 35 – 45 °C • Decomposition temperature: + 80 °C • Half life time: 10 hours at 112 °C, 1 hour at 132 °C and 1 min at 172 °C 	PERGAN GmbH, Bocholt, Germany	Used as received
			
Licocene PP MA 6252 Fine Grain TP (MAPP)	<ul style="list-style-type: none"> • A low molecular, maleic anhydride-modified PP • Graft content of 7% maleic anhydride • Melting point of approximately 140 °C 	Clariant GmbH, Gersthofen, Germany	Used as received
			
Acetone with 99.5% purity	<ul style="list-style-type: none"> • Density of 0.79 g/cm³ • Flash point of < -18 °C; Boiling range of 55.8 – 56.6 °C 	Carl Roth GmbH + Co. KG, Karlsruhe, Germany	Used as received

3.2 Treatment

3.2.1 Impregnation of wood flour



Figure 3.2: Wood flour

Wood flours (Figure 3.2) were dried prior to impregnation in an air-circulating oven at 104 °C until less than 0.1% moisture content was reached. Impregnation was done in a vacuum desiccator according to DIN EN 113 and the impregnation setup is shown in Figure 3.3. Firstly, 2 kg of WF were placed in the desiccator. Then the desiccator was evacuated to less than 10 mbar vacuum. After that coupling agent in isopropanol solution was introduced through the stopcock. The WF was left immersed for three hours before they were taken out and pre-dried in the fume hood for two days to evaporate from the solvent. They were then heated in an air-circulating oven at 104 °C until they reached a constant weight. The impregnation was done with a certain percentage of coupling agents in isopropanol solution for every 2 kg WF as listed in Table 3.2.

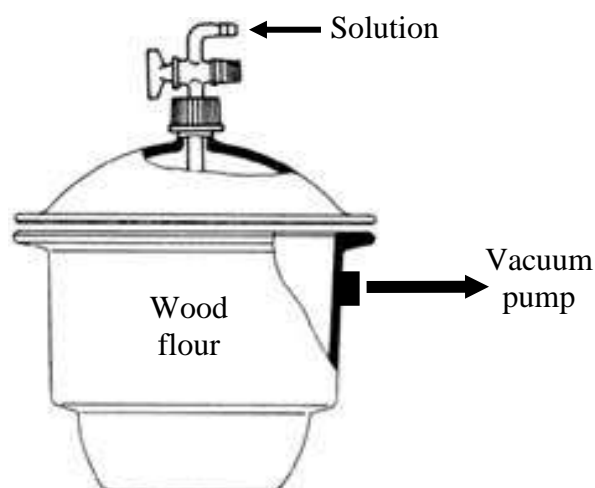


Figure 3.3: Impregnation setup

Table 3.2: List of coupling agent solutions for impregnation

Coupling agent	Percent solution (w/v%)
Tegomer VB 2706 (Triethoxy PDMS)	0, 0.5, 1.0, 2.0, 4.0, 6.0
Tegomer V-Si 4042 (Vinyl PDMS)	0, 0.5, 1.0, 2.0, 4.0, 6.0
50/50 Mixture of Tegomer VB 2706 (Triethoxy PDMS) and Tegomer V-Si 4042 (Vinyl PDMS)	0, 0.5, 1.0, 2.0, 4.0, 6.0
Tegomer V-Si 4042 batch VB 3242 (Bifunctional triethoxy-vinyl PDMS with low molecular weight)	0, 0.5, 1.0, 2.0
Tegomer V-Si 4042 batch VB 3247 (Bifunctional triethoxy-vinyl PDMS with high molecular weight)	0, 0.5, 1.0, 2.0
Tegomer V-Si 4042 batch VB 3248 (Bifunctional triethoxy-vinyl PDMS with very high molecular weight)	0, 0.5, 1.0, 2.0
Tegomer H-Si 2311 (Hydroxyl alkyl PDMS)	0, 2.0, 4.0, 6.0

Table 3.3 gives the equal amount of solvent solution used during impregnation to w/w% treatment on the wood flour. The calculation is shown in the appendix 1, appendixes section.

Table 3.3: Amount of solvent solution (w/v%) to weight percent wood (w/w%) treatment.

Percent solution (w/v%)	Treatment (w/w%)
0.5	1.75
1.0	3.50
2.0	7.00
4.0	14.00
6.0	21.00

The weight percent gain (*WPG*) of wood after impregnation was calculated using the following Equation 3.1 while the coupling agent mass uptake (*MU*) was calculated using Equation 3.2.

$$WPG = \frac{m_{treated} - m_{untreated}}{m_{untreated}} \times 100 \quad (\%)$$

where: $m_{treated}$ = dry mass of wood after treatment
 $m_{untreated}$ = dry mass of wood before treatment

Equation 3.1: Weight percent gain of wood

$$MU = \frac{m_{treated} - m_{untreated}}{m_{solute}} \times 100 \quad (\%)$$

where: $m_{treated}$ = dry mass of wood after treatment

$m_{untreated}$ = dry mass of wood before treatment

m_{solute} = mass of coupling agent in the solution

Equation 3.2: Mass uptake of coupling agent

3.2.2 Pre-mixing

Pre-mixing was done to treat WF or PP with MAPP or to coat the DCP to the grain size PP. This process was done using a thermokinetic mixer type THSK 100, Papenmeier/Lodige, Paderborn. For MAPP treatment the temperature was set to 190 °C with speed of 500 rpm for the first 5 minutes. Then it was increased to 1200 rpm for 20 minutes, and finally it was lower down again to 500 rpm for another 5 minutes. The same processing procedure was followed but with only 45 °C temperatures for coating 0.1% DCP onto the grain size PP.

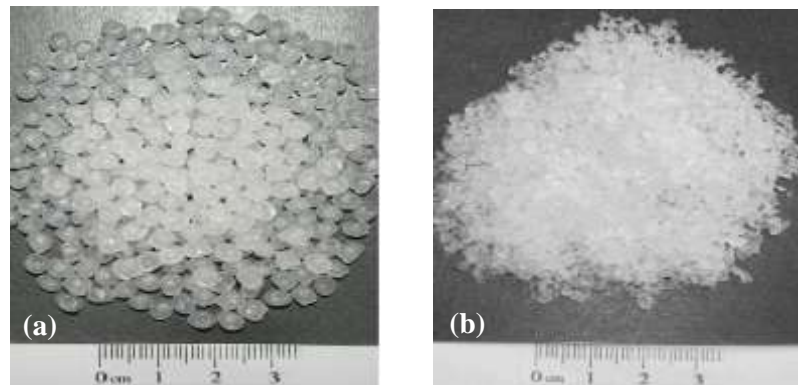


Figure 3.4: Polypropylene (a) original pellet and (b) grain size

3.2.3 Master batch and emulsion

There were two types of coupling agents containing 50 (w/w%) of very high molecular weight bifunctional triethoxy-vinyl PDMS. The first one was the 50% master batch polypropylene (BPP) and the second was emulsion bifunctional triethoxy-vinyl PDMS (em-Bif). The BPP was initially coated with 0.1% DCP in acetone solution using a mechanical stirrer. After all the acetone has been evaporated in a fume hood, a 1.75 wt% BPP calculated to the amount of wood, in the wood plastic composite (WPC) formulation was prepared. The BPP was physically mixed with PP to enable this third material to be fed. This is because only two volumetric

feeding systems were available to be used during processing. However for em-Bif, the treatment was done to the wood flour. It was done by spraying 1.75 wt% coupling agent onto the dried WF surface in a DRAIS dry mixer type ISP 80, DRAISWERKE GmbH, Mannheim-Waldhof for 15 minutes prior to compounding.

3.3 Compounding

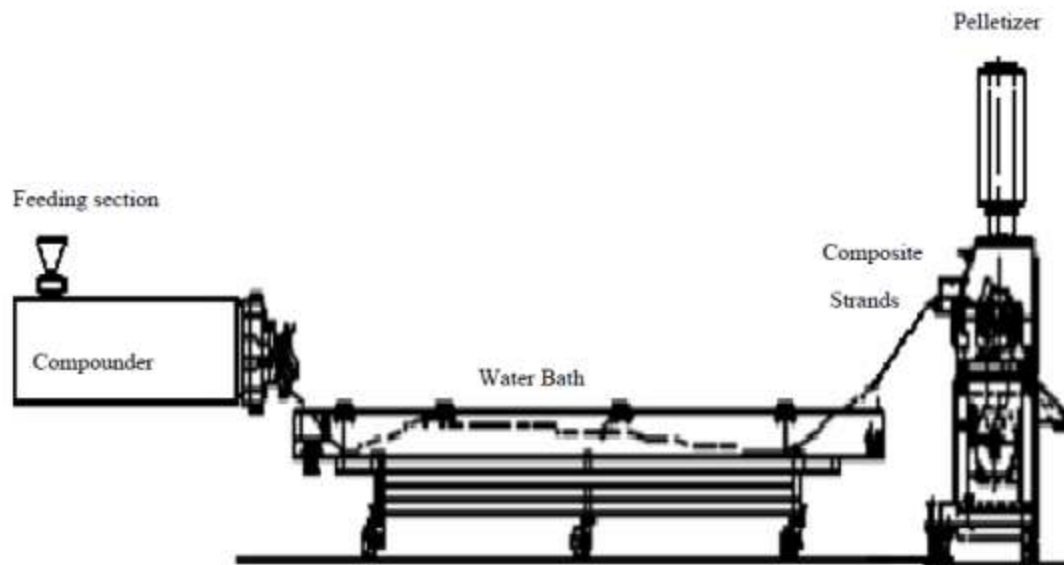


Figure 3.5: Compounding setup

The compounding process was done using a Theysohn co-rotating twin-screw extrusion compounder EKS-TSK 20 Theysohn Holding Ges GmbH, Bad Homburg. The barrel temperatures were set between 150 °C to 193 °C and speed between 180 rpm to 350 rpm depending on the formulation processed (Table 3.4). Prior to compounding wood flours were dried in an air-circulating oven at 104 °C until the moisture content was reduced to less than 1% while polypropylene pellets were ground to grain size using a Condux grinder type LV 15K, CONDEX Hanau-Wolfgang to get a constant flow at a lower feeding rate during processing. Two volumetric feeders type C2S-1/60 kg and type C2S-O/150 kg from Scholz Dosiertechnik GmbH, Niedernberg were used to feed these materials into the compounder. The feeding rates for both feeders were set according to the desired ratios of composites. Both materials were fed through the same feeding section on the barrel. Depending on the type of wood used, the compounding process was done continuously until 1.5 kg to 2 kg composite was obtained. The composite strands were produced from wood flour directly led from the die through the water bath to the Pell-Tec Pelletizer SP 50 Pure from Pell-Tec Pelletizing Tech GmbH, Hanau-Wolfgang and were straightaway pelletized (Figure 3.5). Figure 3.6 shows how the WPC pellets look like. On the other hand, the composite strands produced from wood particles were not pelletized to ensure the original sizes of the wood particles preserved.

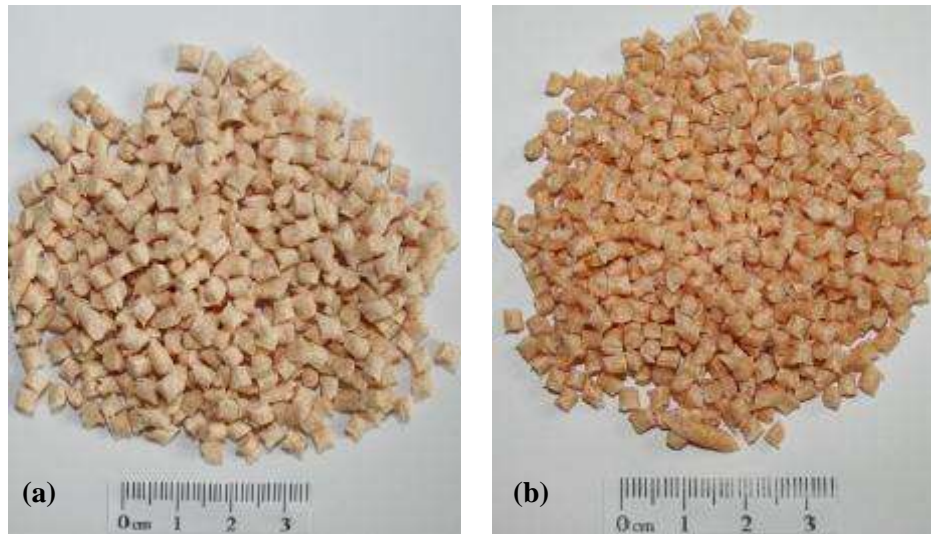


Figure 3.6: WPC pellets with (a) WF/PP 70/30 composition and with (b) WF/PP 30/70 composition

Table 3.4: WPC formulations and the processing conditions

Formulation			Processing condition	
WF/PP Composition (%)	Coupling Agent	DCP (0.1%)	Barrel Temperature (± 3 °C)	Speed (rpm)
70/30	No	No	190, 193, 193, 190	280 - 300
	No	Yes	180, 185, 185, 180	335 - 350
	PDMS	No	160, 165, 165, 165	335 - 350
	PDMS	Yes	150, 155, 155, 155	335 - 350
	MAPP	No	160, 165, 165, 165	300 - 335
50/50	No	No	190, 193, 193, 193	225 - 250
	No	Yes	180, 185, 185, 185	250 - 275
	PDMS	Yes	170, 175, 175, 175	250 - 275
30/70	No	No	190, 193, 193, 193	180 - 200
	No	Yes	185, 185, 185, 185	225 - 250
	PDMS	No	170, 175, 175, 175	285 - 300
	PDMS	Yes	160, 165, 165, 165	285 - 300
	MAPP	No	165, 170, 170, 170	250 - 275

From Table 3.4 we can see that the treated WPC needs lower processing temperature. Every formulation has its own processing profile. This is because the treated formulation will burn if processed with the untreated temperature profile while the untreated formulation will not melt or stuck in the barrel if processed with the treated formulation temperature profile. This is due to the use of a very basic unit of a lab

scale compounder that does not contain a pressure controller to ensure even material flow rate along the barrel during processing. The compounder also does not have any rheology display system to ensure the same processing profile inside the barrel throughout processing. The only possible observation was just from the end product or the strands that come out from the die, which is very subjective.

3.4 WPC panels preparation

WPC pellets obtained from the compounding process were dried in an air-circulating oven at 104 °C until the moisture was reduced to less than 1%. Next, they were ground to flour form (Figure 3.7) using a Condux grinder type LV 15 K, CONDUX Hanau-Wolfgang. The composites' grain was later pressed to 4 mm thickness with a certain target density according to the composition. Every material has its own nature and density. Therefore, compounding two distinctive materials with various compositions will need different target density to maintain the thickness of 4 mm. As described earlier, composite made from bigger/longer wood particle (mid-WP and long-WP) were not pelletized and ground to maintain the sizes. Thus the strands from the die were collected to the amount needed calculated with the same target density as for the wood flour and pressed. Table 3.5 shows the densities used.

Table 3.5: WPC Panels target density

WF/PP Composition (%)	Target density (kg/m ³)
70/30	1250
50/50	1150
30/70	1050



Figure 3.7: Flour form WPC

The panels were melting pressed using Paul Ott hot press machine model 300R-S Spezialmaschinefabrik Paul Ott, Neustadt, Stuttgart. Firstly, the hot press was heated to 180 °C. After that the sample was placed in a square frame made of soft fibreboard in between two metal plates. Next it was placed in the hot press and was pressed until the pressure reached 30 bars and left for 30 minutes. Then the hot press was opened for a few second to remove the moisture content. Later it was pressed again to 100 bars for 10 minutes. Afterwards, once more the hot press was opened to reduce the moisture, and soon it was pressed to 200 bars. After 10 minutes, it was pressed again until the hot press reached the maximum pressure of 275 to 280 bars and subsequently the heater was turned off. The samples with more plastic will be left to cool down to room temperature while the samples with more wood flour will be left for two hours together with the hot press until the temperature reaches 80 °C before it was taken out. The panel is then ready to be cut to the desired size and shape of testing specimens. Figure 3.8 shows the different formulation panels.

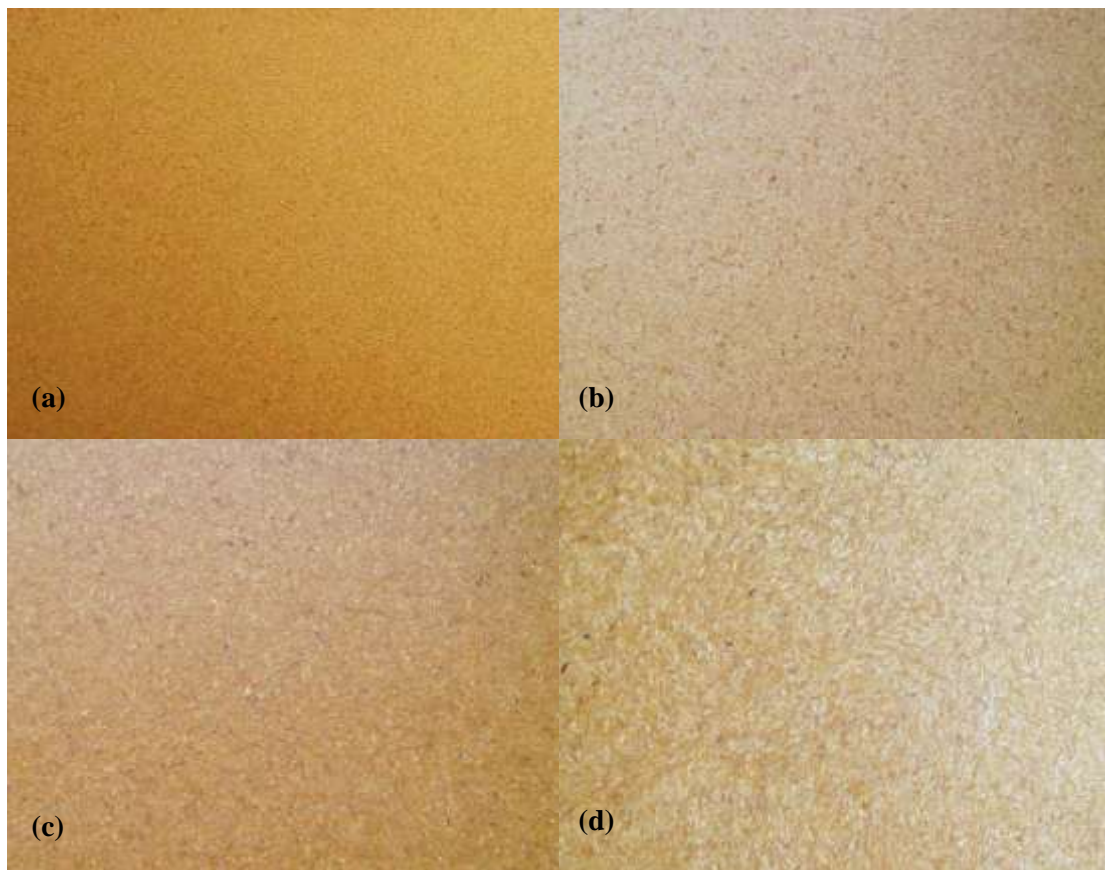


Figure 3.8: WF/PP 70/30 panels with different formulations; (a) without coupling agent (b) with 1.75% very high molecular weight bifunctional triethoxy-vinyl PDMS (c) with 1.75% MAPP and (d) WP/PP 70/30 with particle size of 0.6 – 1.25 mm and treated with 1.75% of 50% master batch very high molecular weight bifunctional triethoxy-vinyl PDMS in PP.

3.5 Testing and analysing

3.5.1 Mechanical properties

Mechanical properties of WPC were determined through the flexural test, tensile test and impact test. The flexural test was done according to the DIN EN ISO 178 standard. The specimens were cut to a dimension of 80 mm x 10 mm x 4 mm and were tested at 2 mm/min of test speed using a three-point bending test until the specimen fractures or until the deformation reaches some predetermined value. The tensile test was done according to the DIN EN ISO 527-1 with the test speed of also 2 mm/min. The specimens were prepared according to DIN EN ISO 527-2 type 1B, which is a dumb-bell-shaped with overall length of 150 mm, measurement width of 10 mm and thickness of 4 mm as shown in Figure 2.8. In this test, the specimen was extended along its longitudinal axis with the gauge length of 50 ± 0.5 mm until the specimen fractures. Both tests were done using Zwick 1474 universal testing machine. However, due to the technical problem during the tensile mode machine, not all the tensile test results could be taken into account.

The impact test was done according to DIN EN ISO 179-1, which is referred to a flatwise impacted unnotched specimen with the dimensions of 80 mm x 10 mm x 4 mm using Zwick D 7900 impact testing machine with 1 J - pendulum. All mechanical testing results were taken from an average reading of at least eight specimens for every formulation. All specimens were placed in the conditioning room at relative air humidity of 65% and temperature of 20 °C prior to testing until they gained less than 1% of weight after 24 hours. The specimens were then weighed to the nearest 0.001 g. Figure 3.9 shows how the specimens were cut out of the panels for testing.



Figure 3.9: Specimens cutting arrangement

3.5.2 Water absorption test

Water absorption was conducted according to DIN EN 317 standard method to determine the swelling in thickness and the dimensional changes of panels. Specimens were measured prior and after a total immersion into water during 28 days. Reading was taken after 24 hours and on the 7th, 14th, 21st and 28th day, from the average measurement of eight specimens' size 50 mm x 50 mm x 4 mm as shown in Figure 3.9.

Water uptake (w) of specimens was determined using the following equation:

$$w = \frac{w_{wet} - w_{original}}{w_{original}} \times 100 \quad (\%)$$

where: w_{wet} = weight after immersion
 $w_{original}$ = initial weight after equilibration at 20 °C and 65% relative humidity.

Equation 3.3: Water uptake calculation

A dimensional change (d) of specimens is referring to the changes in volume and was determined using the following equation:

$$d = \frac{d_{wet} - d_{original}}{d_{original}} \times 100 \quad (\%)$$

where: d_{wet} = dimension after immersion
 $d_{original}$ = initial dimension after equilibration at 20 °C and 65% relative humidity.

Equation 3.4: Dimensional change calculation

3.5.3 Moisture absorption test

Moisture absorption test was done using treated and untreated wood flour at ambient temperature and humidity in the storeroom. 5 g of every sample were weighed and were oven dried at 104 °C for 24 hours. Every formulation was done using three specimens for accuracy. After that, the specimens were analysed for moisture content, and then were left open in the store for 25 days. The moisture content was analysed using Ultra-X moisture analyser model UX 2081. The reading was taken after one hour, five hours, 24 hours, five days and every five days until day 25th.

3.5.4 Thermal analysis

Thermal analysis was performed using a dynamic mechanical analyser (DMA); Tritec 2000, Triton Technology Ltd, Keyworth, United Kingdom in a dual cantilever mode. The specimens were cut to the size of 35 mm x 6 mm x 2 mm and scanned with the dynamic temperature from -40 °C to 120 °C. Sequential frequencies of 0.1 Hz, 1 Hz and 10 Hz were used during measurement with amplitude of 50 µm. Liquid nitrogen was used to cool down the specimen to below -40 °C prior to measurement and the constant heating rate of 2 °C/min was used to collect the data. Four specimens were tested for every formulation.

3.5.5 ATR-FTIR analysis

Attenuated total reflection - fourier transform infrared analysis (ATR-FTIR) was done using a Thermo-Nicolet IMPACT 410 spectrometer, Thermo Fisher Scientific Inc., Germany with OMNIC 2.1 analysis software. Every analysis was run with 32 scans with three specimens of every sample. For treated wood in WPC, the specimens were analysed after soxhlet extraction of the wood flour for 24 hours in xylene solution. The extraction was done to see the existence of covalent bonding between the coupling agent and the wood flour.

3.5.6 SEM/SEM-EDX

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) were performed using SEM Leo 1530 with primary electron energy, E_0 of 1.5 kV and Oxford EDX system with Ge detector. All specimens were sputtered coated with iron prior to analyses for better imaging and two specimens were done for every formulation.

3.5.7 Microscopic image analysis

Microscopic analysis was carried out using Carl Zeiss Axioplan 1, light microscope from Switzerland. WPC panels with 4 mm thickness were cut out to the size of about 10 mm x 15 mm and were put it the hot wax for 15 minutes. After they have cooled, thin slices of 20 µm were microtomed from the waxed specimens. Waxing was done to give better dimensional stability during slicing. The sliced specimens were then submerged in isopropanol for half an hour to dissolve the wax and finally stained with an aqueous solution of 0.5% toluidine blue. Toluidine blue was used to stain the wood with blue colour so that it could be differentiated from the plastic matrices. Next, the specimens were rinsed with water, mounted onto glass slides and covered by cover glass. Three specimens were analysed for every formulation.

3.5.8 Free sugar analysis

Free sugar analysis was done on the 70/30 WF/PP composites with and without 1.75% very high molecular weight bifunctional triethoxy-vinyl PDMS coupling agent. First the composites were ground to a fine powder that could be passed through 0.5 mm sieve using the Condux grinder type V3, CONDUX Hanau-Wolfgang. Then 5 g of the fine powders were extracted in 50 ml distilled water and heat up in an autoclave (CERTO clar Hochdrucksterilisator Traun, Austria) at 120 °C, 1.5 bar for 45 minutes. The solutions were then cooled down to room temperature before they were centrifuged using Eppendorf centrifuge 5412, Hamburg with 11 000 xg speed for 15 minutes. After that the solutions were filtered using Amicon Ultra centrifugal filter Millipore, Ireland with 3 MWCO membranes. The sugar analysis was done using Dionex high performance anion exchange system ICS 3000 chromatograph, USA with pulsed amperometric detection. NaOH was used in the mobile phase column and anion capture CarboPac PA20 in the solid phase column. Every formulation was analyzed using two solvent specimens. The specimens were injected for analysis using an auto-sampling system and were run for 65 minutes with four standard solution calibrations. The following method was used during the analysis.

Eluent:	1: Water
	2: 20 mmol/l NaOH
	3: 500 mmol/l NaOH
Flow:	0.4 ml/min
System pressure:	30 MPa
Detector:	IPAD
Temperature:	30 °C
Injection volume:	10 µl

3.5.9 Overall processing procedure

The following figure shows the schematic of overall processing procedure in producing the composites as has been done in this doctorate thesis

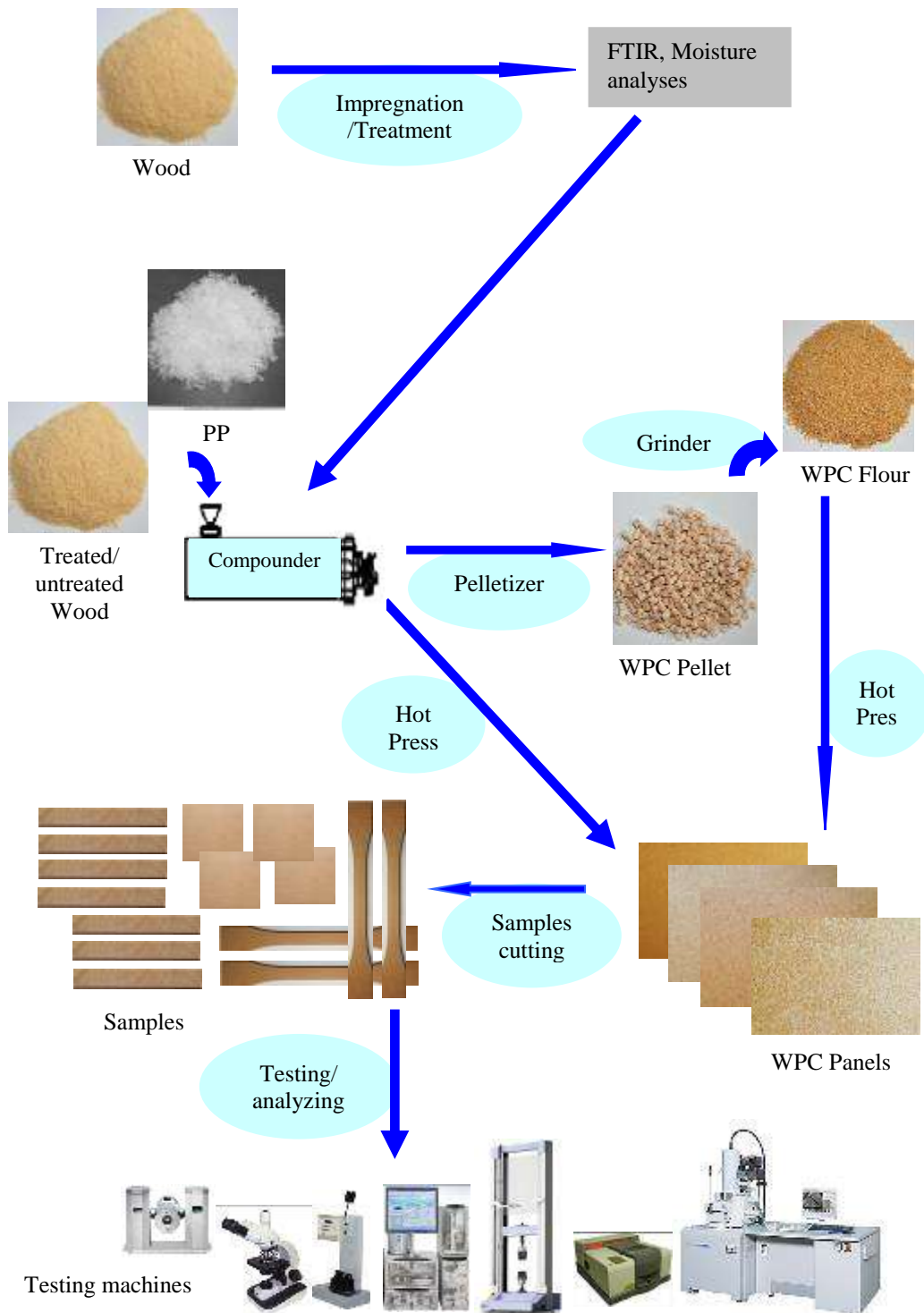


Figure 3.10: Overall processing procedure

4 Influence of the coupling agent amount on the performance of WF/PP composites

One of the factors influencing the performance of WPC is the amount of treatments used in the formulation. The structure and properties of the interphase change with the amount of coupling agents used (Ishida & Miller, 1984). Too much or as well too little coupling agent will not have a positive effect on the performance. Thus optimization is necessary in order to achieve maximum efficiency. Throughout this research, a trend on the optimum range of the treatment amount has been found, which improves the performance of the WPC.

First, the composites were produced using wood flour treated with single functionality PDMS coupling agents. Here vinyl PDMS (TEGOMER V-Si 4042) and triethoxy PDMS (TEGOMER VB 2706) and 50/50 percentage mixture of both vinyl PDMS and triethoxy PDMS coupling agents were used. Then, bifunctional coupling agents with different molecular weight were used to treat the wood flour, here the bifunctional triethoxy-vinyl PDMS with low molecular weight, high molecular weight and very high molecular weight distribution were used. The wood was impregnated with 1.75, 3.5, 7.0 and 14.0 wt% coupling agents. The impregnation procedure was described in Chapter 3, section 3.2.1. Weight percent gain (*WPG*) of coupling agent after impregnation was calculated using the Equation 3.1 (in Chapter 3) while the coupling agent mass uptake (*MU*) was calculated using Equation 3.2 (in Chapter 3). The results of the *WPG* and *MU* are as listed in Tables 4.1 and 4.2.

The composites were then prepared with 70/30 WF/PP compositions using 0.1 wt% dicumylperoxide (DCP) as the radical initiator. 70 wt% wood flour filled PP polymer was in focus of the research because it is well known that wood flour is cheaper than PP and that there are abundant of it as waste materials. The use of DCP in WPC has been reported to vary from 0.1 to 0.75% what depends on the formulation use (Nachtigall *et al.*, 1999 & 2007; Bengtsson *et al.*, 2006 & 2007; Bengtsson & Oksman, 2006; Mokoena *et al.*, 2004, Azizi & Ghasemi, 2004; 2005). There is no report on the specific amount of DCP used with a particular material. They always vary because every formulation will have its own properties. Several trials were done to determine appropriate amount of DCP. All trials with DCP and the influence in WF/PP systems will be discussed in the next chapter. The Figures 4.4 to 4.7 give a better view on how much treatment is needed to improve the properties of 70/30 wood flour/polypropylene composites.

4.1 Weight percent gain and mass uptake

Table 4.1: Weight Percent Gain

Treatment (w/w%)	Weight Gain (w/w%)					
	V-Si 4042	VB 2706	50/50 V-Si 4042/VB 2706	V-Si 4042 VB 3242	V-Si 4042 VB 3247	V-Si 4042 VB 3248
1.75	1.2	1.6	1.4	1.2	1.4	1.5
3.50	3.3	2.7	2.5	3.3	2.9	3.2
7.00	6.7	6.3	6.2	6.0	5.5	6.3
14.00	10.8	11.9	10.5	9.9	12.6	10.1

Table 4.2: PDMS uptake

Treatment (w/w%)	Mass Uptake (w/w%)					
	V-Si 4042	VB 2706	50/50 V-Si 4042 + VB 2706	V-Si 4042 VB 3242	V-Si 4042 VB 3247	V-Si 4042 VB 3248
1.75	69.0	91.0	80.0	69.0	80.0	88.0
3.50	94.0	77.0	71.0	94.0	83.0	90.0
7.00	95.0	90.0	88.0	86.0	79.0	90.0
14.00	77.0	85.0	75.0	71.0	90.0	72.0

Legend: V-Si 4042 is Vinyl PDMS, VB 2706 is Triethoxy PDMS, V-Si 4042 VB 3247 is low molecular weight bifunctional triethoxy-vinyl PDMS, V-Si 4042 VB 3247 is high molecular weight bifunctional triethoxy-vinyl PDMS and V-Si 4042 VB 3248 is very high molecular weight bifunctional triethoxy-vinyl PDMS.

As shown in Tables 4.1 and 4.2, more than two third of every coupling agent used were gained during the impregnation process ranging from 69% to 95% mass uptake were recorded. The impregnation procedure was successfully done with quite a very high efficiency of mass uptake observed. However, the treatment containing 14% coupling agent also gives about the same percentage of mass uptake, maybe because too much coupling agent has caused in a higher viscosity of solution thus making it harder to impregnate the wood fibre.

These results show that the coupling agents might have filled in the wood flour's cell wall and lumen (Hill, 2006). The coupling agents might have taken the water places at the cell wall because they have been removed following the drying process prior to impregnation. During impregnation, hydrolysis of triethoxy functionality (for triethoxy PDMS or bifunctional PDMS) may take place and hydrogen bonding may have occurred between the PDMS hydroxyl groups and wood hydroxyl groups. Covalent bonds will be generated between PDMS and the wood

during drying (Hill, 2006; Bengtsson *et al.*, 2005 & 2006). For the vinyl PDMS, no covalent bonding may occur to the wood. However, the reaction may exist through interdiffusion and polymer chain entanglement between the vinyl PDMS chain and the amorphous part of the wood as has been reported by Pizzi (1994). Hull (1995) stated that interdiffusion might be promoted by the presence of a solvent. Therefore, this mechanism may take place during the immersion of wood in the solvent solution of vinyl PDMS.

4.2 FTIR analysis

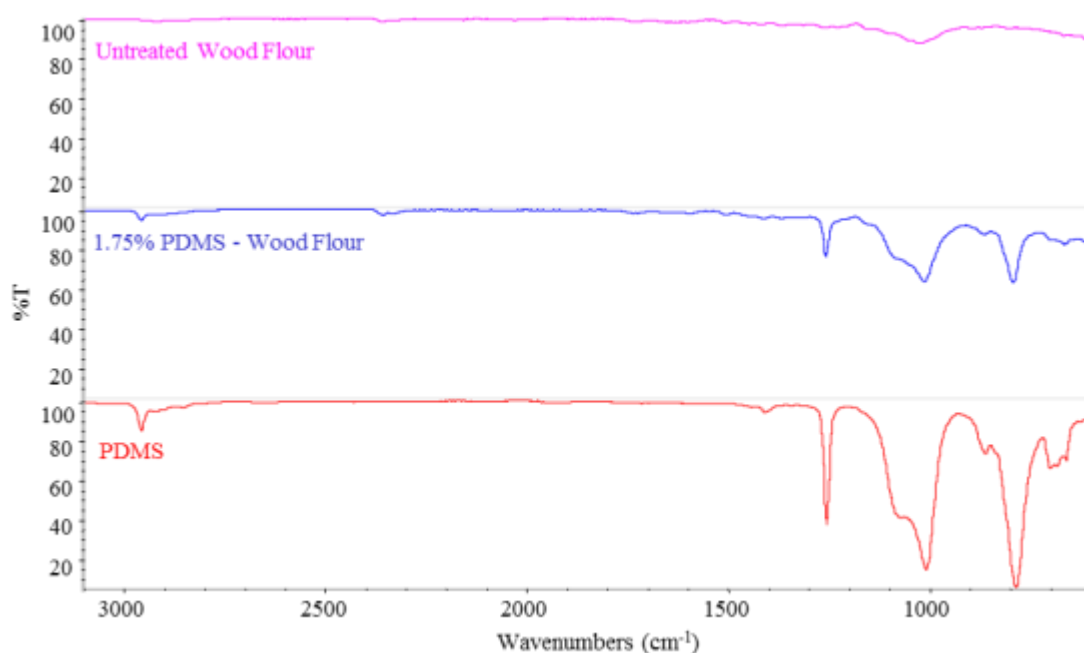


Figure 4.1: FTIR spectrum of 1.75% triethoxy PDMS treated wood compared with the untreated wood and triethoxy PDMS.

FTIR analysis has been done to see the existence of the PDMS after impregnation, and the results are shown in Figures 4.1 and 4.2. From the comparison made in Figure 4.1, we can see that the treated wood spectrum contains the combination of both untreated wood spectrum and PDMS spectrum. All the other treatments exhibit the same spectrum (Figure 4.2).

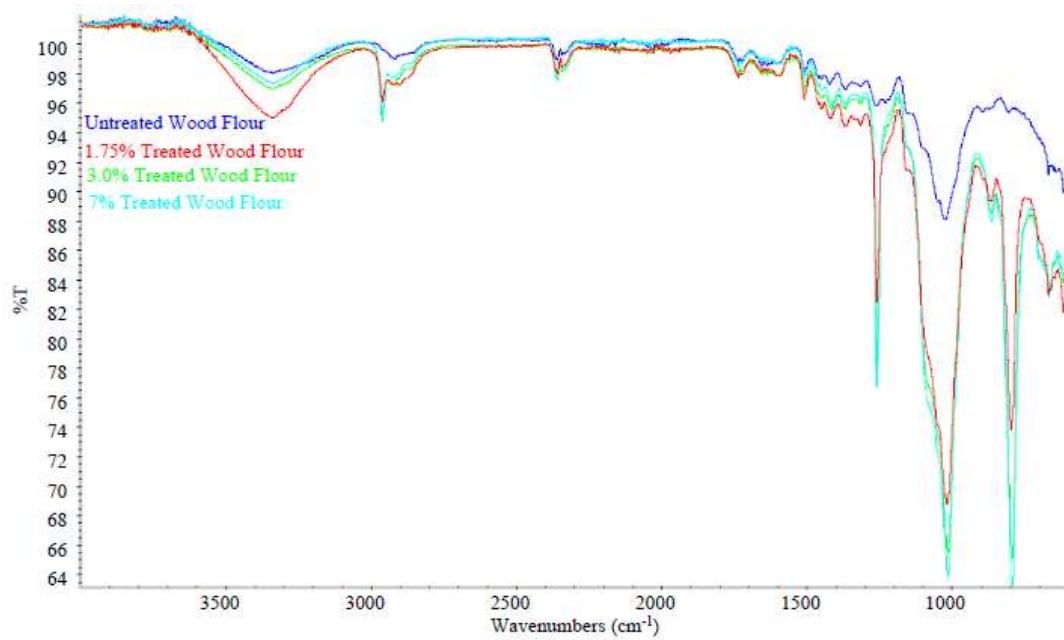


Figure 4.2: FTIR spectrum of different triethoxy PDMS treatment concentration

4.3 Moisture absorption

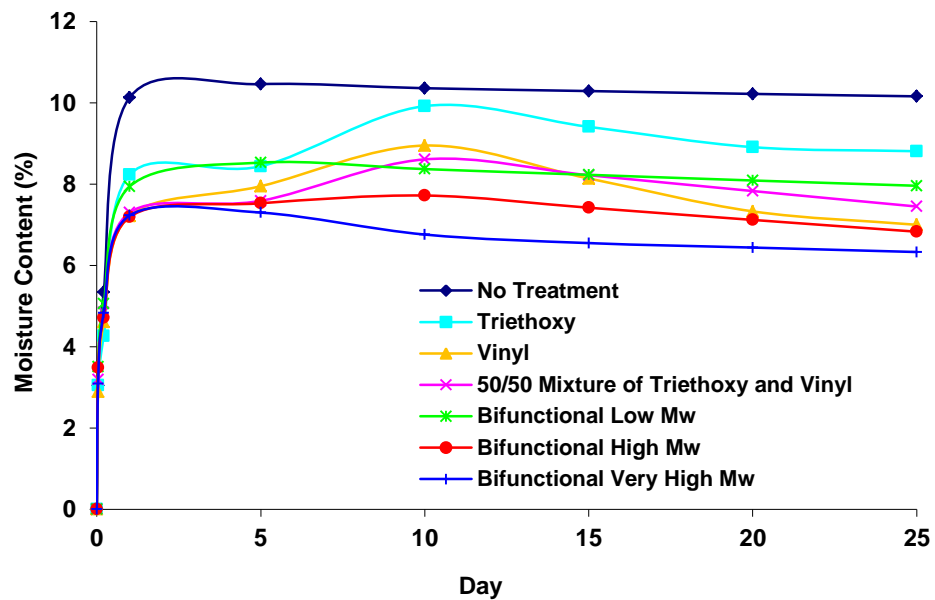


Figure 4.3: Moisture absorption of wood flour under ambient temperature with 1.75% of different PDMS treatment in the matter of time.

Moisture absorption test has also been done to examine the effect of PDMS treatment on the hygroscopicity of the treated wood. The treated wood was first dried

in the air circulation oven over the period of 24 hours and then the moisture content was taken. After that the treated wood were left open in the storeroom for 25 days with the moisture content measurement taken at a certain scheduled time. The method is described in detail in Chapter 3, section 3.5.3. As we can see from Figure 4.3, all treated wood shows a reduction in the moisture uptake if compared to the untreated wood flour. The most effective treatment was with very high molecular weight bifunctional PDMS. Almost 40% decrement was observed compared to the untreated wood flour. These results verified that PDMS has occupied spaces within the cell wall that would otherwise be available to water molecules, which leads to a reduction in the hygroscopicity of the wood (Hill, 2006). Diffusion of water and other molecules into the cell wall were also reduced because PDMS might have blocked the cell wall micro pores effectively, which also leads to the reduction in hygroscopicity. These results also show that PDMS has exhibited the hydrophobicity characteristics.

4.4 Mechanical properties

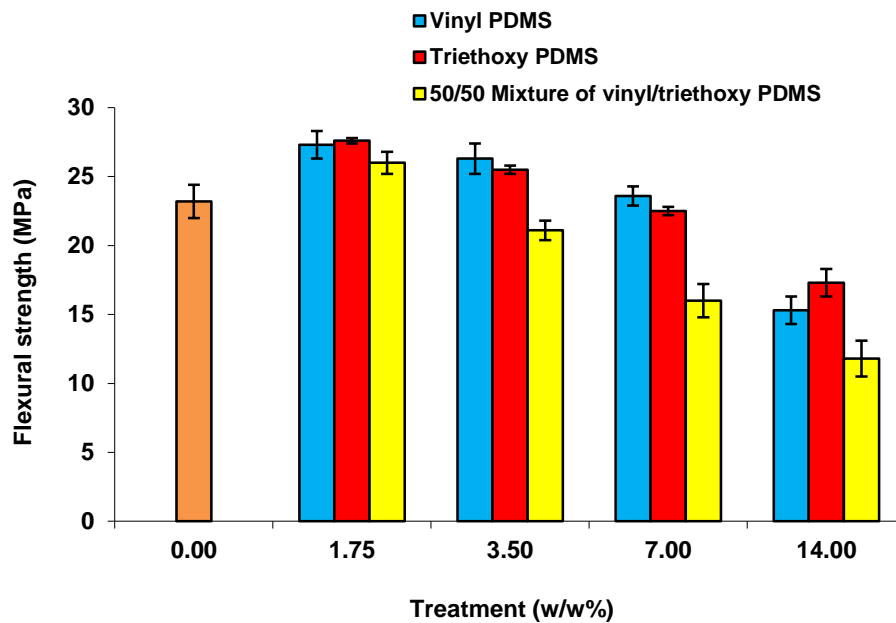


Figure 4.4: The effect of treatment amount on the flexural strength of WF/PP 70/30 with different types PDMS coupling agent

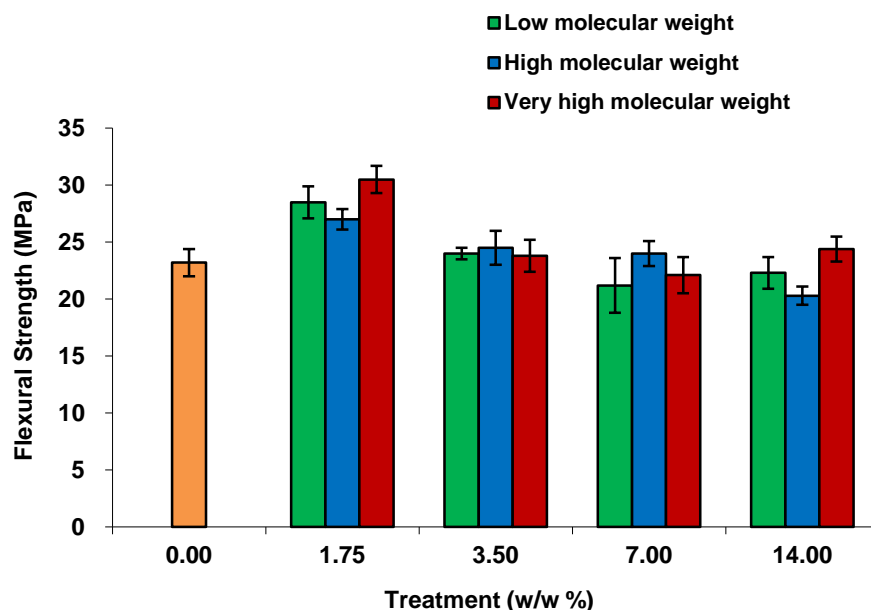


Figure 4.5: The effect of treatment amount on the flexural strength of WF/PP 70/30 with different bifunctional triethoxy-vinyl PDMS molecular weight

Figures 4.4 and 4.5 show the effect of treatment amount on the flexural strength. With 70/30 WF/PP compositions, we can see that by introducing of around 2% PDMS coupling agents into the systems, the flexural strength increased compared to untreated composites for all six different coupling agents. Increasing the amount of coupling agents above 2% up to 14% either decreased the flexural strength with the increments of single functionality PDMS or decreased and then level off at a certain value with the increments of different molecular weight bifunctional PDMS. The optimum amount of PDMS coupling agent is appeared to be 1.75%. There are several factors affecting composites strength such as filler volume fraction, filler aspect ratio, filler orientation, adhesion of wood and plastics, filler properties, matrices properties and processing conditions (Hofse, 1996). Here, the additions of PDMS coupling agents as low as 1.75% have significantly improved the adhesion between wood and PP matrices. The strength decreased after further increments of PDMS because too much PDMS caused them to exhibit plasticizers characteristic or work as a softening agent. Plasticizers work by embedding themselves between the chains of polymers, spacing them apart (increasing the "free volume"), and thus significantly lowering the glass transition temperature for the plastic and making it softer. This means that it will be more flexible, though its strength and modulus will decrease pursuant to it (Biron, 2007). Furthermore polysiloxane also listed to be used as plasticizer (Wypych, 2004) and has been patented by Ishikawa *et al.* (2000) to work well in plasticizing rubber composites. The flexibility of the composites at a high amount of coupling agent could even be seen if the composites strands were just barehanded bend. They could be bent to a further extend compared to the composites with 1.75% treatment.

The same trend could also be seen for the composites' modulus of elasticity in Figures 4.6 and 4.7. The most effective amount of treatment is as well 1.75% for all six different coupling agents used. The optimum modulus of elasticity is also achieved at 1.75% of coupling agent. For the single functionality PDMS, the modulus of elasticity of the 50/50 mixture shows the highest value compared to vinyl PDMS and triethoxy PDMS. This is only comparable to the lowest modulus of elasticity for the 1.75% bifunctional PDMS. This result shows that bifunctional PDMS works better in our WF/PP composites and 1.75% of coupling agent is the optimum amount for our system. Further discussion on functionality performance is presented in Chapter 6.

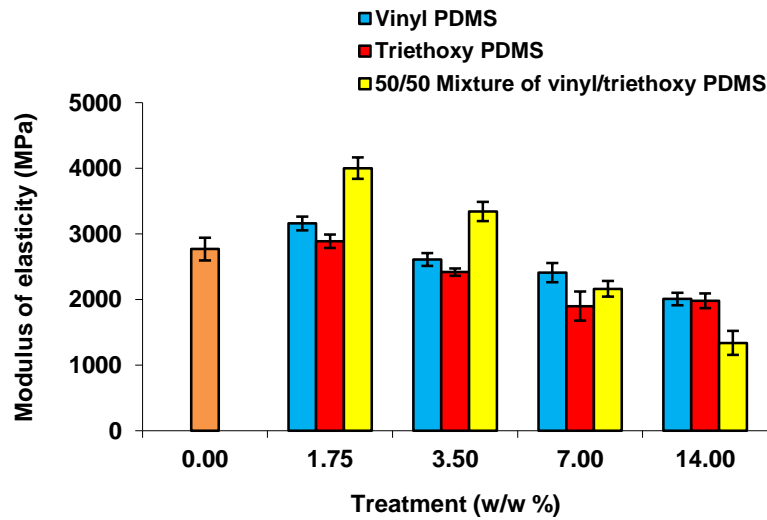


Figure 4.6: The effect of treatment amount on the modulus of elasticity of WF/PP 70/30 with different types PDMS coupling agent

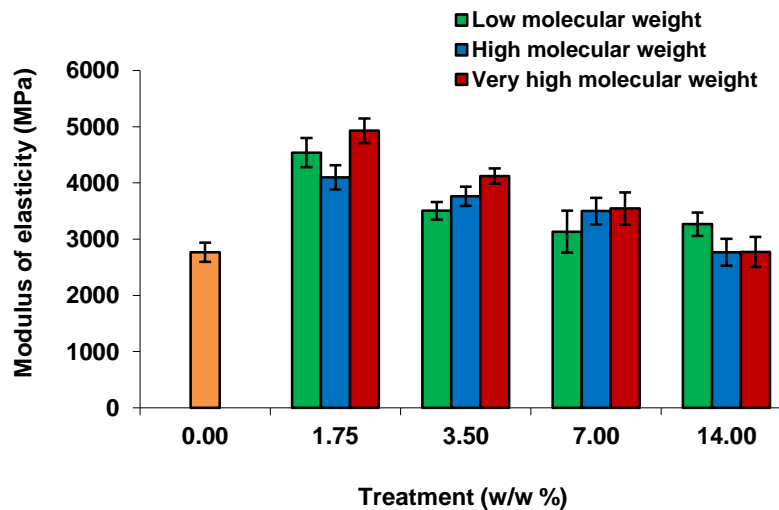


Figure 4.7: The effect of treatment amount on the modulus of elasticity of WF/PP 70/30 with different bifunctional triethoxy-vinyl PDMS molecular weight

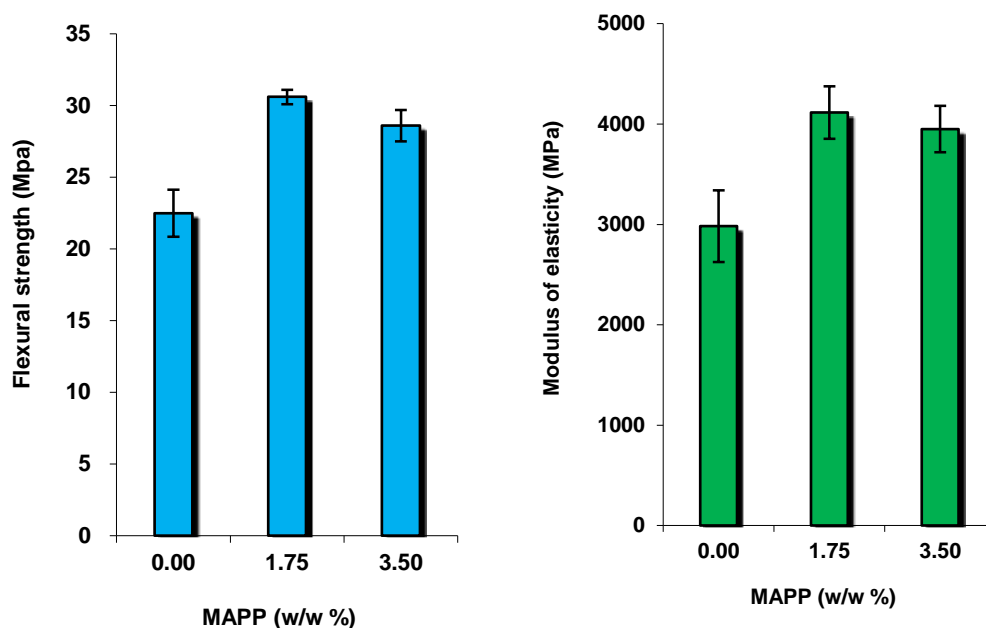


Figure 4.8: The effect of MAPP treatment amount on the flexural strength and modulus of elasticity of WF/PP 70/30

Commercial MAPP coupling agent has also been used in this research as a comparison to standardize the result with the industrial composites' performance. Further discussion on the comparison will be seen in Chapter 7. MAPP was used and processed with the same method of processing except that it was not impregnated but pre-mixed with the PP before compounding. From Figure 4.8 we can see that the flexural strength and modulus of elasticity are higher when only 1.75% of MAPP compared to 3.5% MAPP was used. The strength and stiffness of the composites decreased when 3.5% MAPP was added. Both PDMS and MAPP show a similar optimum amount in our system. The MAPP result is identical to the results reported by Maldas and Kokta (1991) who also used MAPP only up to 3% of the weight of wood fibre used and Dalvag *et. al.* (1985) found that 3% MAPP gives the optimum improvement in strength and both used HDPE/wood composites systems. They also reported that further addition of MAPP does not result in further improvement in strength.

Further investigation has been made focusing on the amount in between the optimum amount to ensure that 1.75% coupling agent is really optimal for our composites system. 0.88% and 2.63% of coupling agent has been included for our set of trials using 50% master batch very high molecular weight bifunctional triethoxy-vinyl PDMS in PP coupling agent to see the effectiveness. This is the same bifunctional PDMS coupling agent we have been using but in different condition. Previously, they were in a liquid form and were applied using impregnation but this coupling agent is already compounded in the PP as a 50% master batch. This coupling agent was used to compare the effectiveness of different condition coupling agent and method of application on our composites performance. Further discussion

on the comparisons will be given in Chapter 8. The following Figure 4.9 shows the results.

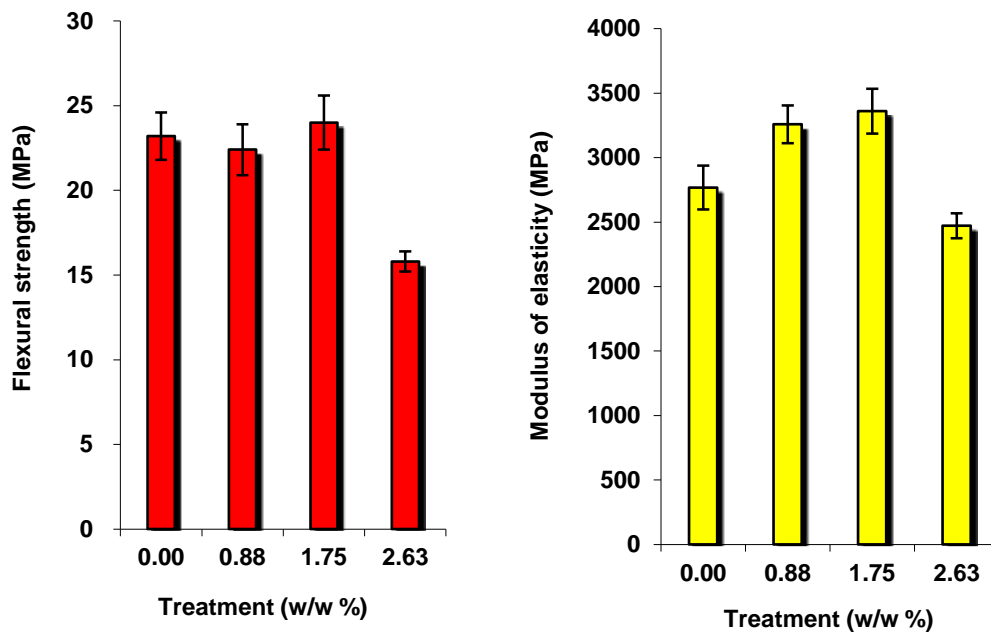


Figure 4.9: The effect of the treatment amount on the flexural strength and modulus of elasticity of WF/PP 70/30 treated with 50% master batch very high molecular weight bifunctional triethoxy-vinyl PDMS compounded in polypropylene.

From Figure 4.9 we can see that the flexural strength of the composites has its optimum at 1.75% coupling agent and decreases with further increments of treatment, as shown with 2.63% coupling agent used. Even though the increment is not so significant compared to the untreated composites, but we can still see the same trend. 0.88% coupling agent is most probably too little to react effectively with the wood and the matrix. The amount is not enough to perform wetting at the interface but exist only as impurities, which interrupted or destroyed the interaction of the polypropylene-wood interface. Their presence caused the strength to decrease even lower than the composites without a coupling agent. On the other hand, the modulus of elasticity increased with the addition of coupling agent and it also has its optimum at 1.75%. The modulus of elasticity of the composites does not decrease but increased with 0.88% coupling agent. The 0.88% maybe too little to effectively adhere the interface but their presence may have improved the homogeneity of the composites and increased the stiffness.

From the overall results, we can see that the 70/30 WF/PP composites have improved and gained the optimum strength and stiffness with the addition of 1.75% coupling agent. These results show that with 1.75% coupling agent interaction between woods – coupling agent – PP is the most effective. With such an amount the coupling agents is able to form effectively an interphase and bridge the wood and the PP matrix together.

5 Influence of DCP initiator to WF/PP systems

Radical initiators are substances that can produce free radicals and promote radical reactions. Normally, these substances are used in polymer synthesis, polymerization reaction or polymer cross linking process. Typically, radical initiators are halogen molecules, azo compounds and organic peroxides. In this research, dicumylperoxide (DCP) was used to initiate the bonding reaction between vinyl groups from the coupling agent and the PP chain. DCP has been reported to give the best result as a radical initiator in grafting of maleic anhydride on polyethylene compared to the other radical initiators such as benzoyl peroxide (BPO) or azobisisobutyronitrile (AIBN) (Ghaemy & Roohina, 2003). Maldas and Kokta (1991) also reported that DCP reacted better than benzoyl peroxide (BPO) as the initiator in MA-HDPE/wood composites system. It degrades relatively quickly compared with other peroxides, requiring only a few minutes to decompose to half of its mass at common processing temperatures. More time is needed for other peroxides with longer half-times-lives for decomposition/initiation (Tolinski, 2009). Therefore, DCP has widely been used in various WPC processings (Nachtigall, *et al.*, 1999 & 2007; Azizi *et al.*, 2008).

5.1 Amount of DCP

At the beginning of this research, as much as 2% DCP have been used in the WF/PP composites as suggested by PERGAN GmbH (through their experience in the field), the supplier of the DCP. Their suggestion was that DCP could be used in WPC from 2% to 5%. However, from the results obtained (Figure 5.1) it can be seen that the use of DCP gave no improvement to the composites' strength. 2% DCP was too much producing too many peroxy radicals thus increasing the probability of chain scissors of PP polymer during processing (Azizi *et al.*, 2008). This could be seen in the effect of lowering the impact strength (Figure 5.2) as a result from the PP becoming less elastic and when less energy was absorbed by composites (Azizi *et al.*, 2008). Furthermore, the composites containing 2% DCP gave a very strong unpleasant smell of DCP, which was probably coming from the excess DCP that did not react during processing. The smell could spread to the whole lab room after a few hours the composites were left open. Therefore, another trial was done with a lower amount of DCP, which was just 0.5%. The results were more or less, still the same.

As stated in Chapter 4, the use of DCP in WPC has been reported to vary from 0.1 to 0.75% depending on the formulation used, but no specific amount has been reported to be used with a particular system and processing condition. The aforementioned results proved the theory that every system has its own properties

and characteristic, which will need an individual recipe and formulation. Optimization of compound used must be realized. Therefore, a set of tests to figure out the optimum amount of DCP and to enhance the properties of WF/PP itself were done, which later would be used with the PDMS coupling agent. The following figures will give a clearer view on the role played by the initiator, especially to the mechanical properties of plastic itself.

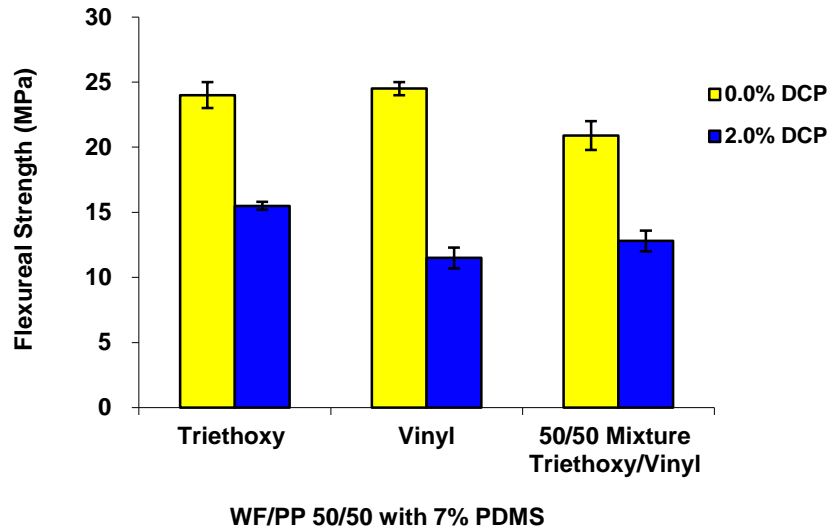


Figure 5.1: The effect of 2% DCP on flexural strength of WF/PP 50/50 with different PDMS treatment

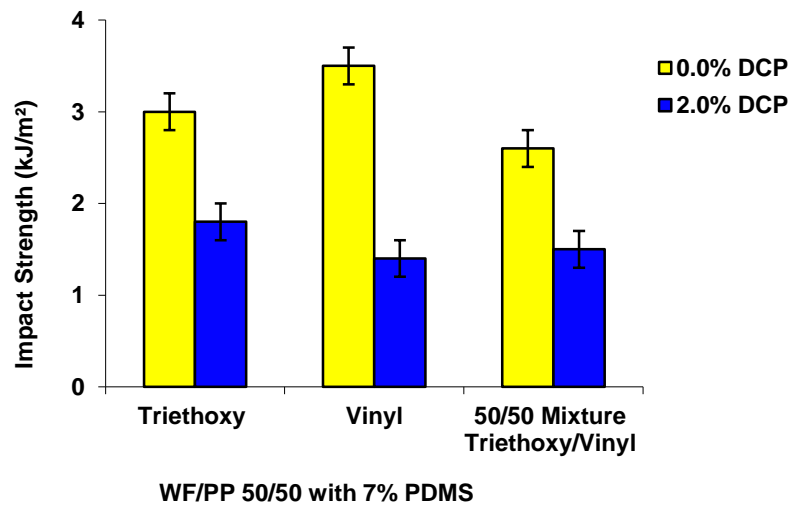


Figure 5.2: The effect of 2% DCP on impact strength of WF/PP 50/50 with different PDMS treatment

5.2 Effect of DCP on flexural strength of different PP compositions

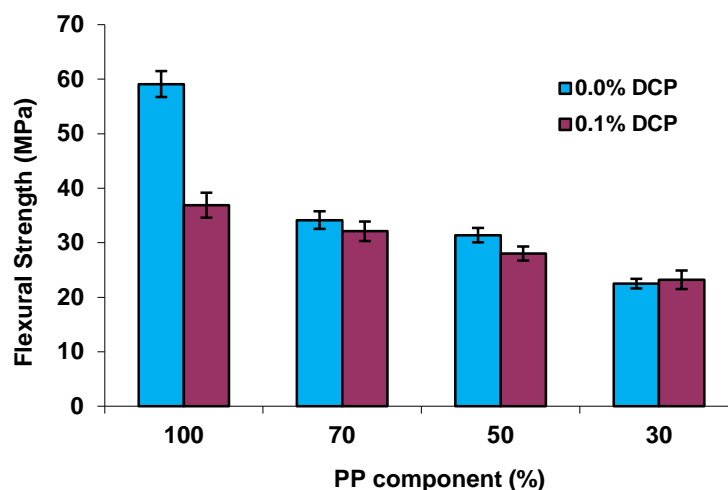


Figure 5.3: The effect of DCP on flexural strength of WF/PP composites with decreasing composition of PP component

As can be seen in Figure 5.3, the addition of 0.1% DCP has decreased around 35% of the flexural strength for the pure unfilled PP plastic. Further decrements can be seen with the composites' results. The decrements of PP composition in the composites itself have reduced the flexural strength and with the addition of 0.1% DCP in the composites systems caused further decrements on the flexural strength. It is obvious that the effect of DCP is more prominent to the PP polymer than to the composites.

The decrement in the strength for the PP filled wood flour composites system compared to the unfilled PP can be attributed to the addition of inert particulate fillers to a plastic system. They do not contribute to the enhancement of the strength but their presence is just enough to fill the void within the PP polymer and increase the stiffness of the trial product. PP also does not have any reactive group in the structure to react chemically with the wood. Furthermore, the homogeneity and compatibility conflict of both wood and PP materials contributed to the lowering of the strength, as well. Increasing the filler loading decreases the strength because of the wetting problem. There are not enough PP matrices to adhere to the wood and form an interface. This also leads to the increased number of micro voids caused by the larger amount of the poorly bonded area between the hydrophilic filler and the hydrophobic matrix polymer (Yang *et al.*, 2006).

DCP is normally working as an initiator to induce polymerization or cross-linking in a polymer compound. DCP will decompose during processing at a suitable temperature to give cumyloxy radicals that can react directly with another polymer or by further decomposition to form acetophenone and methyl radicals (Parks & Lorenz, 1961) (Figure 5.4). Bremner & Rudin (1993) reported that these radicals work well to give rise to cross linking in polyethylene. However, PP contains tertiary carbon atoms occurring alternately on the chain backbone, which is particularly

susceptible to oxidation at elevated temperatures. PP will degrade under this condition to form lower-molecular-weight products (Chanda & Roy, 2007). Shorter, low-molecular-weight polymer chains have fewer statistical chances of cross-linking with other chains (Tolinski, 2009). Furthermore, Tolinski (2009) has stated that less-branched polymers and polymers with methyl groups such as PP tend to be more susceptible to degradation from unwanted chain scission (breakage), rather than cross linking and the addition of DCP to PP had more tendencies in promoting degradation during processing (Azizi & Ghasemi, 2004). That is why 0.1% DCP caused the strength to decrease.

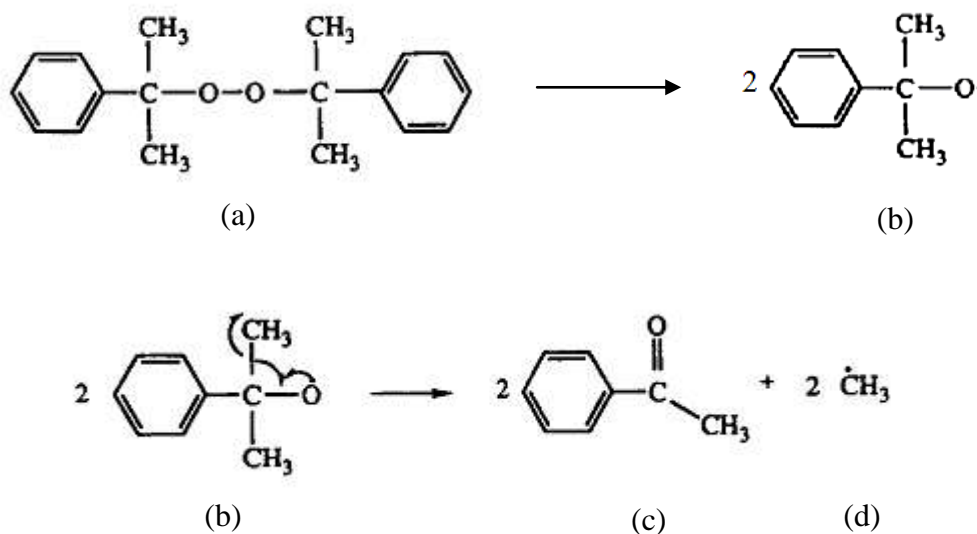


Figure 5.4: (a) DCP (b) cumyloxy radicals (c) acetophenone and (d) methyl radicals

5.3 Degradation and DMA analysis of glass transition temperature

Degradation of PP chain by the addition of 0.1% DCP can be proven by looking at the glass transition of DMA (Figure 5.5). The glass transition temperature (T_g) indicates the relaxation in a polymer where a material changes from glassy to rubbery. It is also known as “the melting of the amorphous phase”, which is the temperature range where a material softens (PerkinElmer, 2008). How soft or hard a polymer is at a given temperature, is determined by what is called chain mobility, that is, how well the polymer chains wiggle past and around each other. The more they can move, the softer the polymer is.

The glass transition is taken from the loss modulus peak. It has been reported by Li *et al.* (2000) that the T_g is more consistent if the value is based on the loss modulus peak. We can see that the glass transition of the WPC with 0.1% DCP has shifted to a lower temperature compared to the one without DCP. This is because the shorter PP chains produced by the DCP reaction are more mobile compared to the original long PP that could be entangled. Shorter chain will produce more free volume in the polymer, thus provides more space for the chain to move. This result

also proved that 0.1% DCP has caused chain scission rather than crosslinking in the PP.

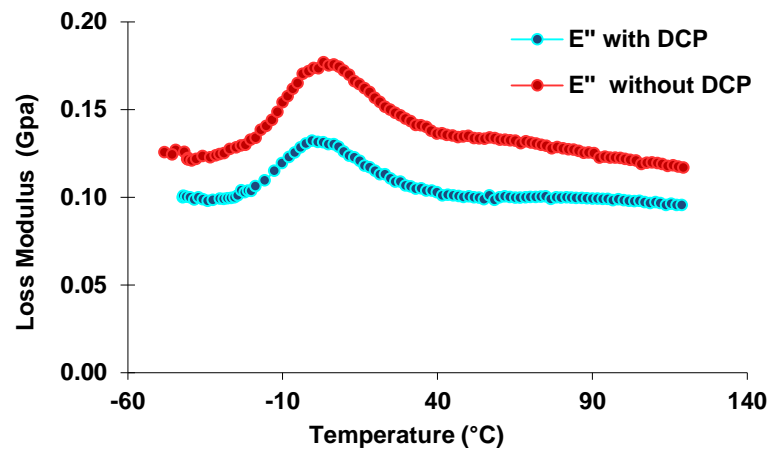
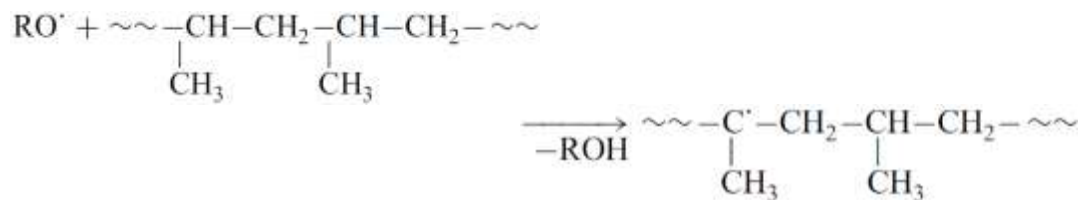
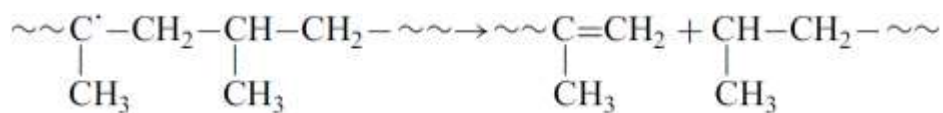


Figure 5.5: T_g of the loss modulus for WF/PP 70/30 with and without 0.1% DCP

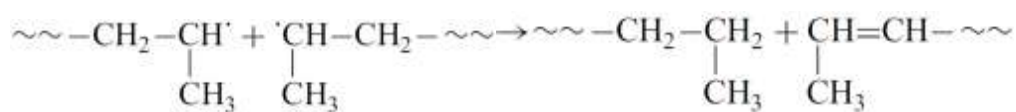
The following mechanism is reported in Bash and Karian (2003) to occur during degradation of PP in an extruder. The first step of the mechanism involves generation of peroxy radicals $\text{ROOR} \rightarrow 2\text{RO}^\bullet$ through thermal decomposition of peroxide, as shown in Figure 5.4. The radical then attacks the backbone of the polymer, abstracting tertiary hydrogen:



The backbone then degrades by beta scission:



The polymeric radicals then terminate by disproportionation:



5.4 Effect of DCP on Modulus of elasticity and impact strength with different PP compositions

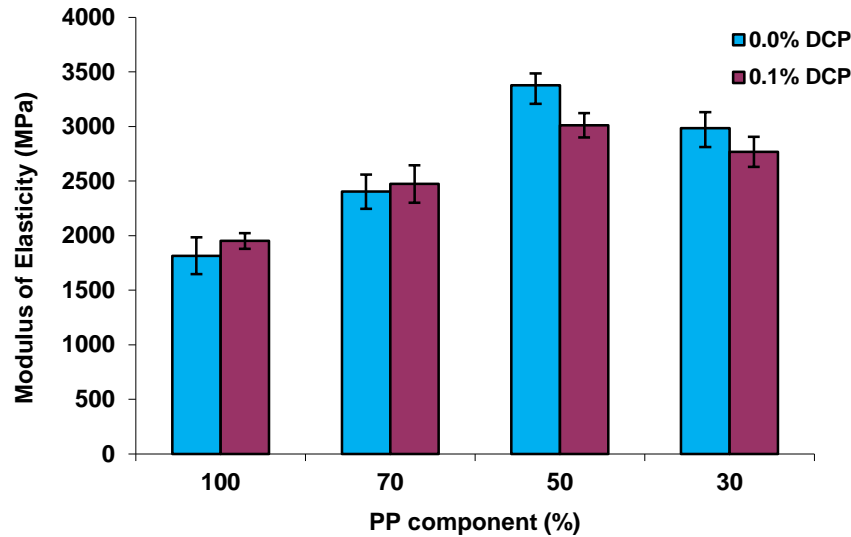


Figure 5.6: The effect of DCP on modulus of elasticity of WF/PP composites with decreasing composition of PP component

As discussed, the stiffness of the composites would be higher than the unfilled PP plastic, a normal phenomenon when a matrix is filled with inert filler. Adding of 0.1% DCP to the unfilled PP and composites with 30% wood caused some increment in the modulus of elasticity while the effect to the composites with 50% and 70% wood flour is lowering the modulus of elasticity. The increment in the modulus of elasticity of unfilled PP and composites with high PP content is due to the higher crystallization as results of chain scission (Maier & Calafut, 1998). It is easier to form crystal with shorter chain length (Azizi & Ghasemi, 2004; Maier & Calafut, 1998). However, the crystallization effect cannot be seen when more wood was used in the composites system.

Impact strength depends directly on the molecular weight of the polymer (Ibhadon, 1998). Thermal degradation or chain scission generally involves changes in the molecular weight or molecular weight distributions. The effect of lower molecular weight on the impact strength can clearly be seen in Figure 5.7. The impact strength of the unfilled PP is obviously decreased when 0.1% DCP was added, showing the effect of chain scission on PP plastic. The decrement of impact strength is also observed in the composites. This is due to the lower elasticity and lacked in interconnection in the composites to absorb energy, following shorter PP chain length with the addition of DCP.

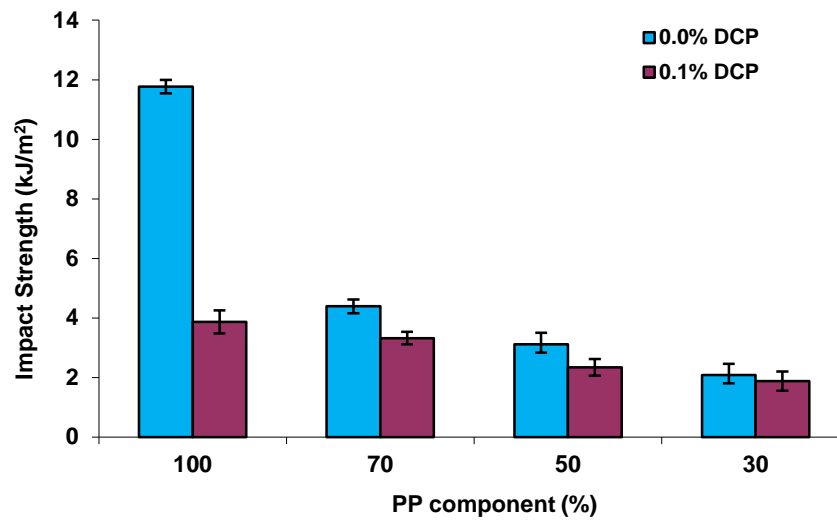


Figure 5.7: The effect of DCP on impact strength of WF/PP composites with decreasing composition of PP component

5.5 DCP contents with different WF/PP compositions

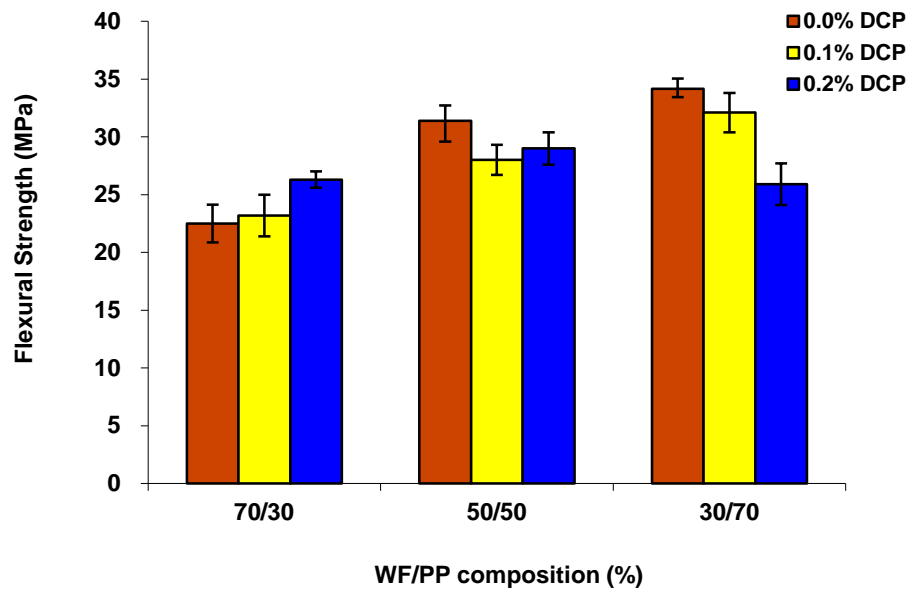


Figure 5.8: The effect of DCP on flexural strength of WF/PP composites with three different compositions

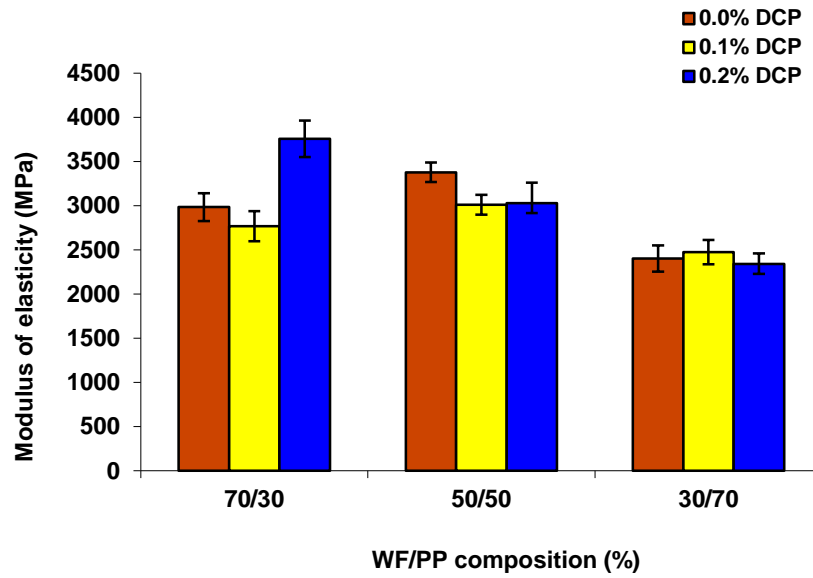


Figure 5.9: The effect of DCP on modulus of elasticity of WF/PP composites with three different compositions

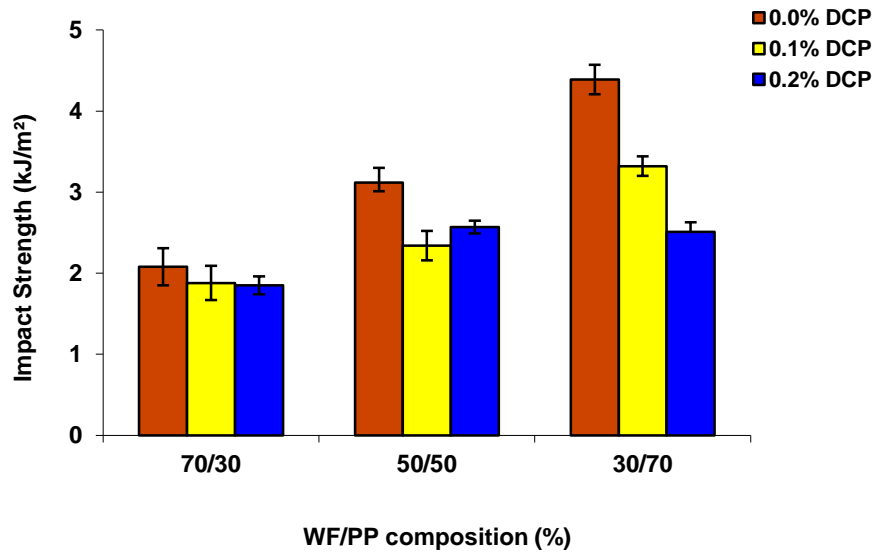


Figure 5.10: The effect of DCP on impact strength of WF/PP composites with three different compositions

Figures 5.8 to 5.10 give the comparisons when more DCP was used in three different WF/PP composites systems. Increasing DCP content to 0.2% has decreased the strength of composites containing 70% PP but increased with composites containing lower PP content. These results show that the existence of more free radicals during processing caused more chain scission in PP and the effect is more significant when more PP plastic compounded in the composites. These results can

be further supported by the composites impact strength, which also shows decrement when DCP concentration was increased.

The free radicals initiated by the DCP may also abstract hydrogen from cellulose. The hydrogen abstraction in cellulose may occur from –OH and C-H of the cellulose backbone as well as from methylol (-CH₂OH) groups (Sapieha *et al.*, 1990). On the other hand, in PP the free radicals may take place at tertiary carbon (Sapieha *et al.*, 1990; Azizi *et al.*, 2008). The increasing of flexural strength with the increases DCP used showed that the free radicals have also attacked the cellulose fibre and grafting of cellulose-PP may have taken place and overcome the chain scission effect giving raised to the composites strength. The same results can be seen in the composites' modulus of elasticity where 0.2% DCP has increased the modulus of elasticity of composites with 70% wood.

However, even though the strength was enhanced with 0.2% DCP the unpleasant smell of DCP was still there. This is probably due to the unreacted DCP in the composites. The DCP has a half-life of one minute at 172 °C and of one hour at 132 °C. Even so, the retention time in the compounder during processing was only 30 seconds, which means that increasing DCP concentration leads to more unreacted DCP. That is why 0.1% DCP has been chosen to be used in the composites.

5.6 DCP as a radical initiator of the very high molecular weight bifunctional triethoxy-vinyl PDMS

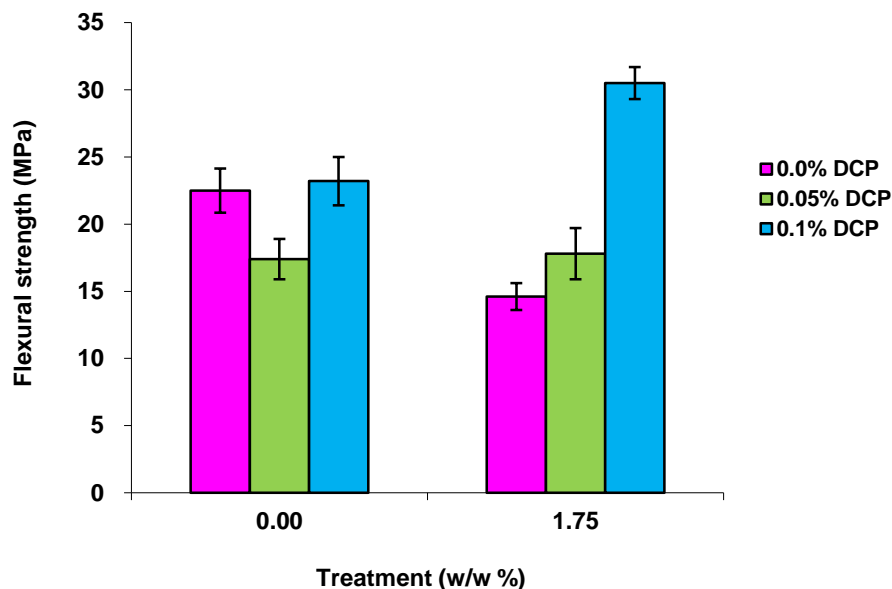


Figure 5.11: The effect of DCP on flexural strength of 70/30 WF/PP with and without 1.75% very high molecular weight bifunctional triethoxy-vinyl PDMS

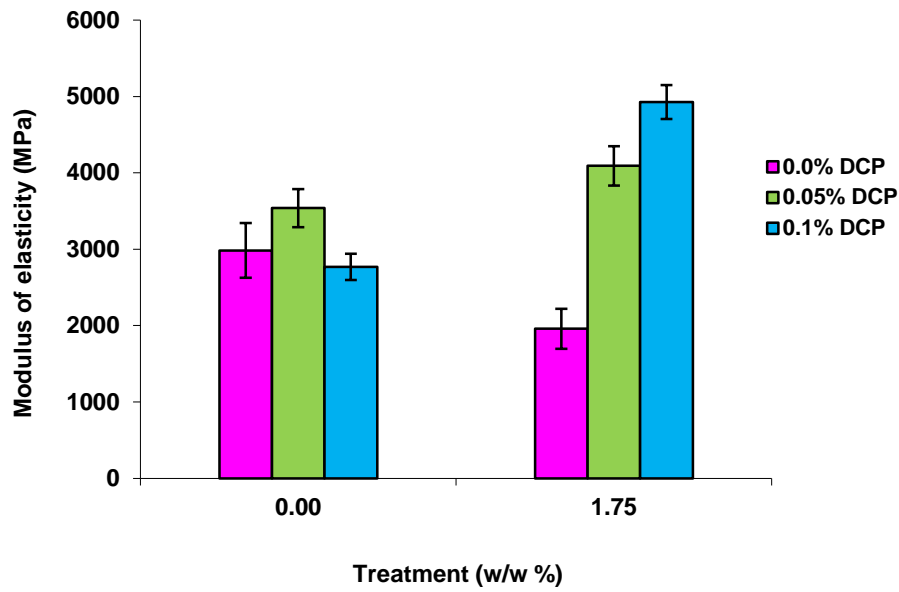


Figure 5.12: The effect of DCP on modulus of elasticity of 70/30 WF/PP with and without 1.75% very high molecular weight bifunctional triethoxy-vinyl PDMS

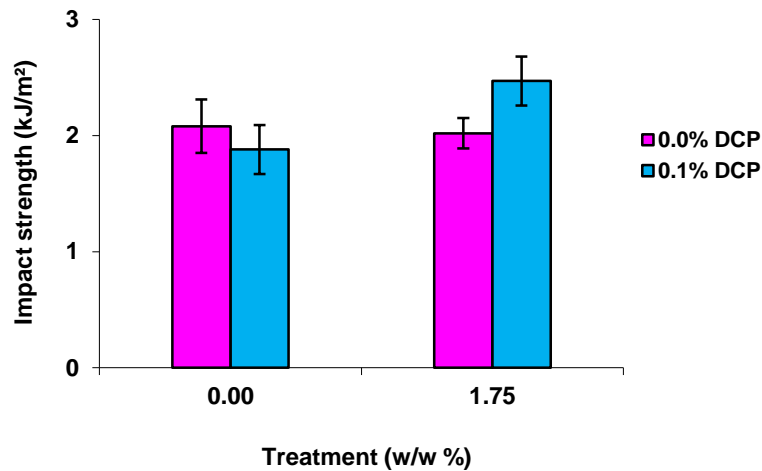


Figure 5.13: The effect of DCP on impact strength of 70/30 WF/PP with and without 1.75% very high molecular weight bifunctional triethoxy-vinyl PDMS

Further work has been done focusing on our main research topic, which is the use of PDMS coupling agent in enhancing the performance of 70/30 WF/PP composites. 1.75% of PDMS coupling agent has been chosen, and we have double-checked the amount of DCP to be used in our composites to a lower concentration to see the effectiveness. From Figures 5.11 to 5.13 we can see the enhancement of the strength, modulus of elasticity and also the impact strength of composites containing

0.1% DCP. The use of 0.1% DCP has as well reported by Azizi *et al.* (2005, 2008) to be the optimum concentration of DCP as a radical initiator in a PP system.

The addition of 1.75% of very high molecular weight bifunctional triethoxy-vinyl PDMS into the composites has decreased the mechanical properties of composites compared to the untreated compound. This shows that the treatment only gives negative effect to the composites system. However, when the treatment was used together with the DCP radical initiator, about 35% of the flexural strength and 75% of the modulus of elasticity increased compared to the untreated composites. Nevertheless, impact strength also shows some increment. These results show that some chemical reactions and bondings have occurred during the process. The existence of the vinyl group in PDMS coupling agent may lead to the formation of covalent bonding with the PP and as discussed in Chapter 4, the formation of covalent bonding between the triethoxy group from PDMS and hydroxyl groups from wood might have occurred during impregnation. They have formed a strong interface between wood and PP and as well created an interphase to bridge the compound. Further discussion on the functionality reaction could be seen in the next chapter.

5.7 SEM and SEM-EDX analysis of very high molecular weight bifunctional triethoxy-vinyl PDMS treated composites with 0.1% DCP

SEM has been used to see the difference in the micrographs of the flexural fractured surfaces of treated and untreated composites and processing with and without DCP. Besides, the SEM-EDX has also been used to identify the elemental chemical composition of the specimen and the distribution of PDMS in the composites. The following Figure 5.14 shows the micrographs of the composite systems.

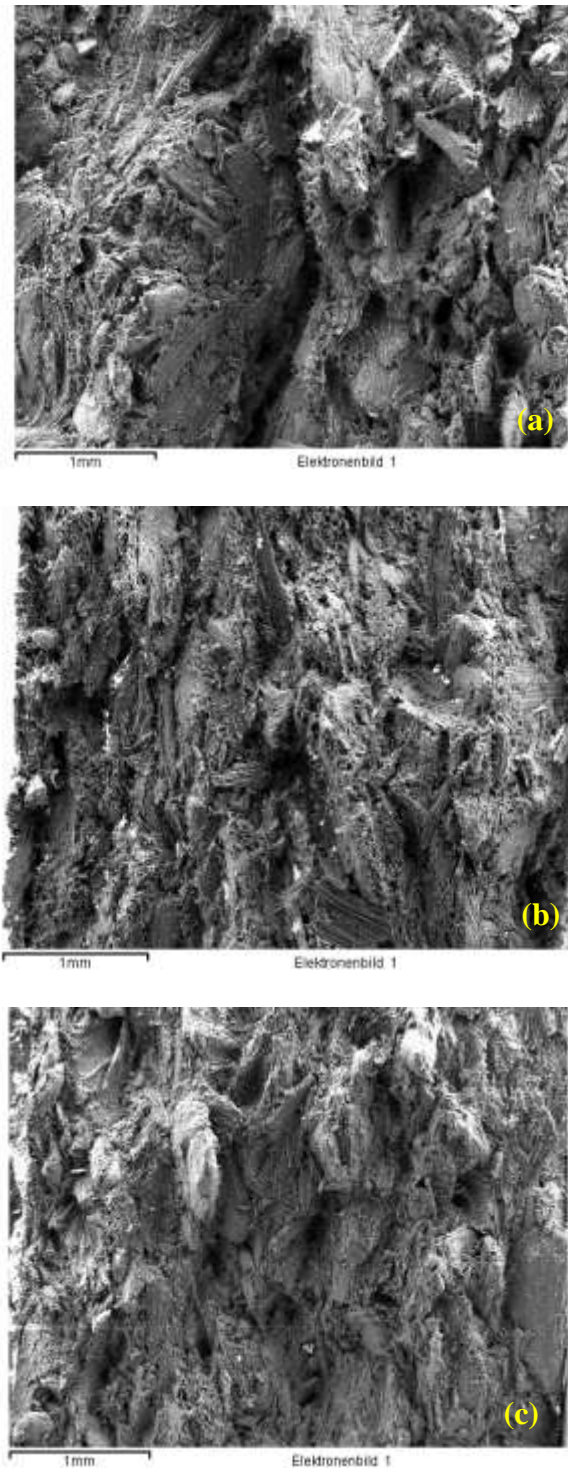


Figure 5.14: SEM micrographs of WF/PP 70/30 (a) without treatment, (b) with 1.75 very high molecular weight bifunctional triethoxy-vinyl PDMS with 0.1% DCP and (c) with 1.75 very high molecular weight bifunctional triethoxy-vinyl PDMS without DCP

As we can see from the micrographs, no significant difference could be detected between these three different formulations. Too much wood in the

composites caused difficulties even to distinguish between wood and PP polymer matrices. Following these results we have made another attempt by polishing the cross section of the specimen. However, this effort did not bring any success either. We still cannot recognize any differences from the micrograph as shown in the following Figure 5.15.

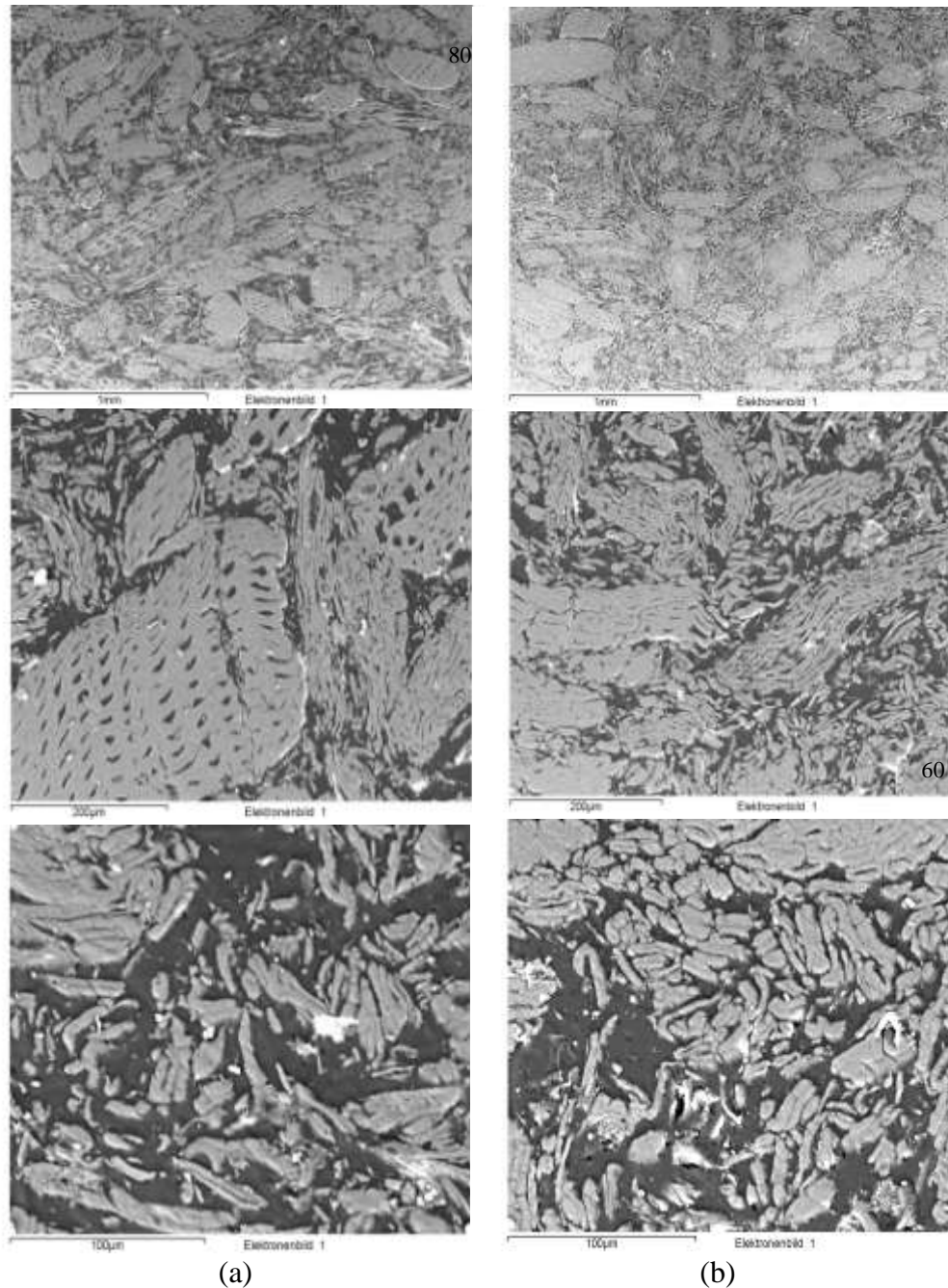


Figure 5.15: SEM micrographs of WF/PP 70/30 (a) without treatment and (b) with 1.75% very high molecular weight bifunctional triethoxy-vinyl PDMS and 0.1% DCP

The following Figures 5.16 and 5.17 shows the SEM-EDX micrographs used to identify the elemental chemical composition of the specimen.

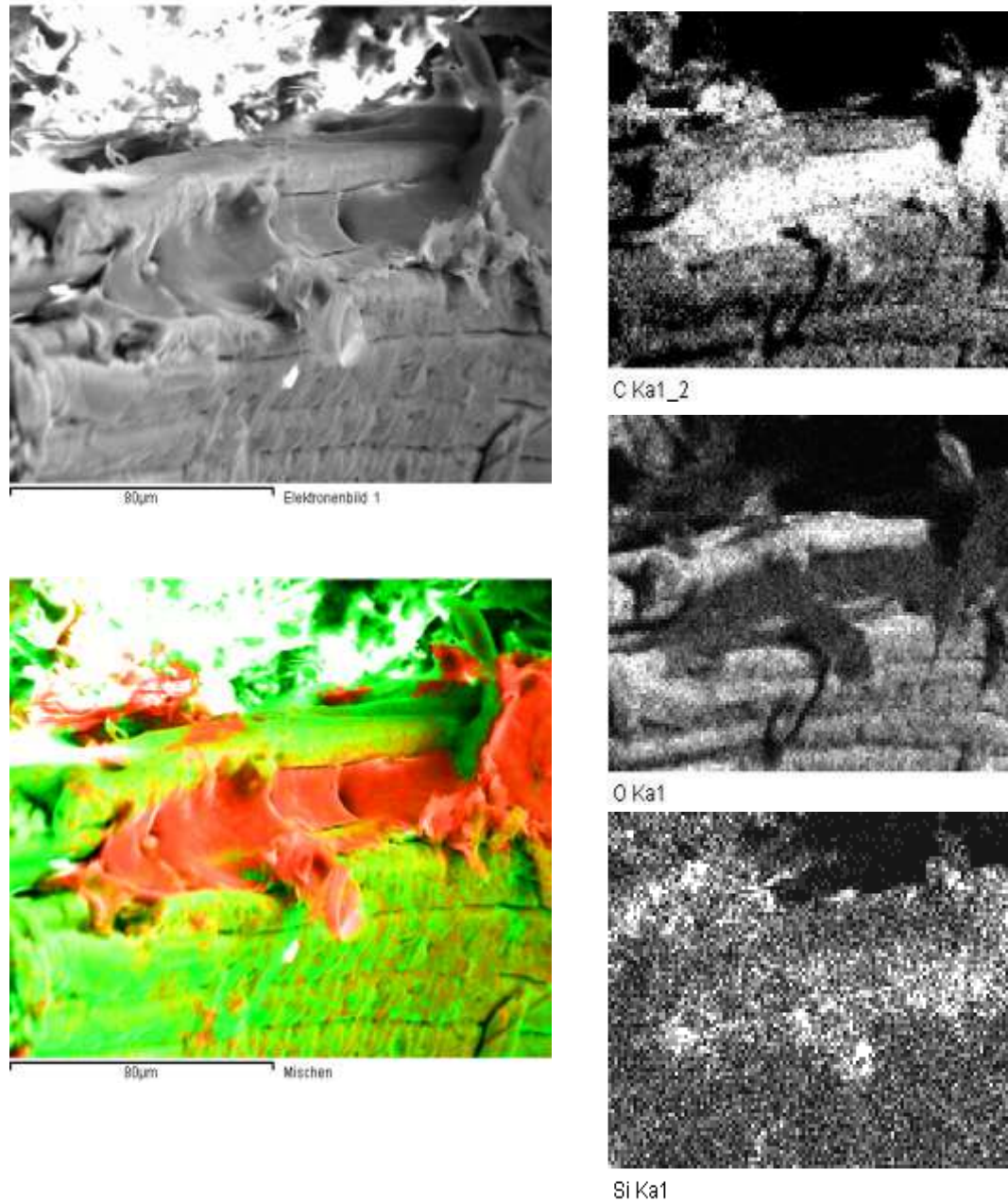


Figure 5.16: SEM-EDX micrographs of WF/PP 70/30 with 1.75% very high molecular weight bifunctional triethoxy-vinyl PDMS with 0.1% DCP

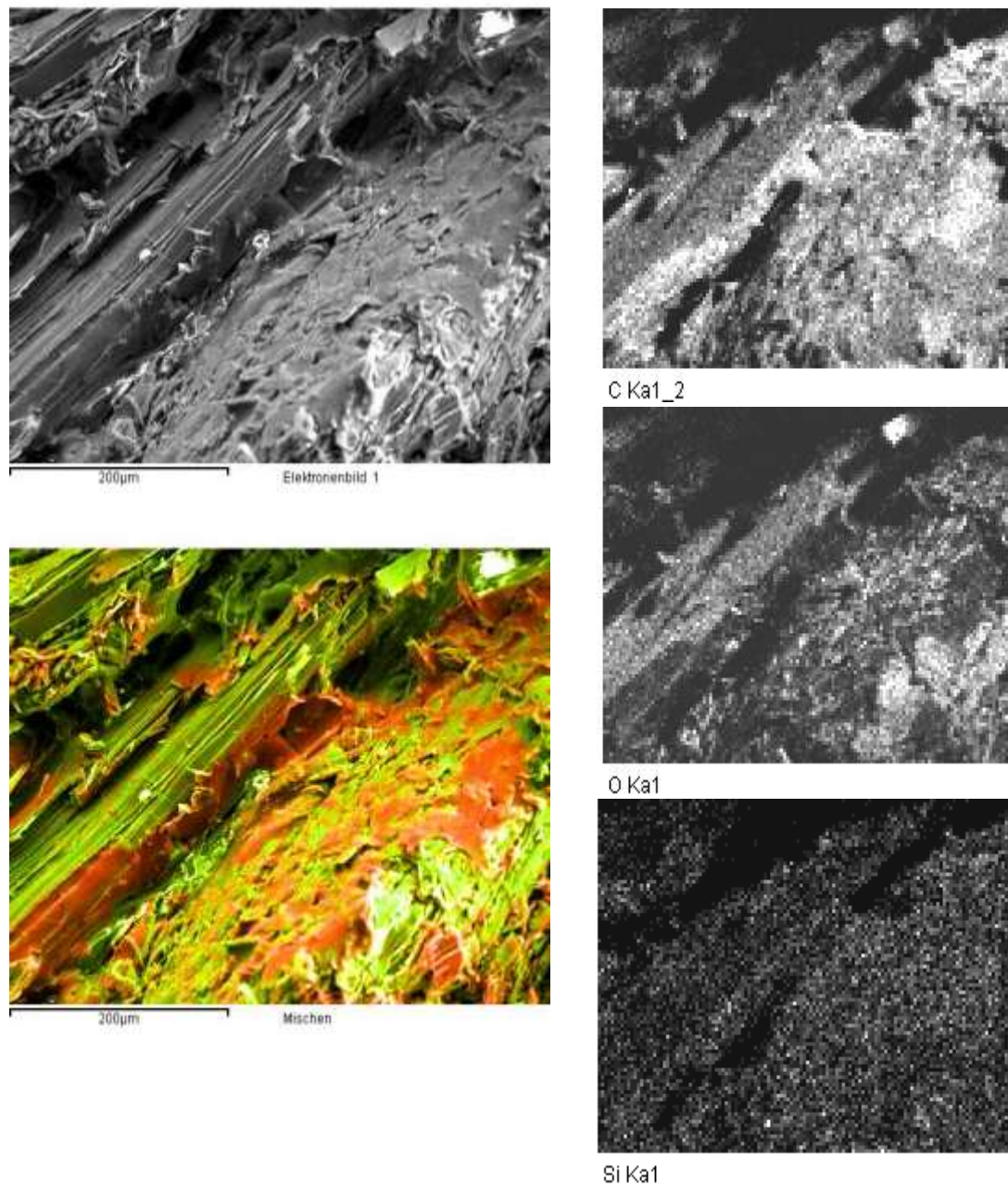


Figure 5.17: SEM-EDX images of WF/PP 70/30 with 1.75% very high molecular weight bifunctional triethoxy-vinyl PDMS without DCP

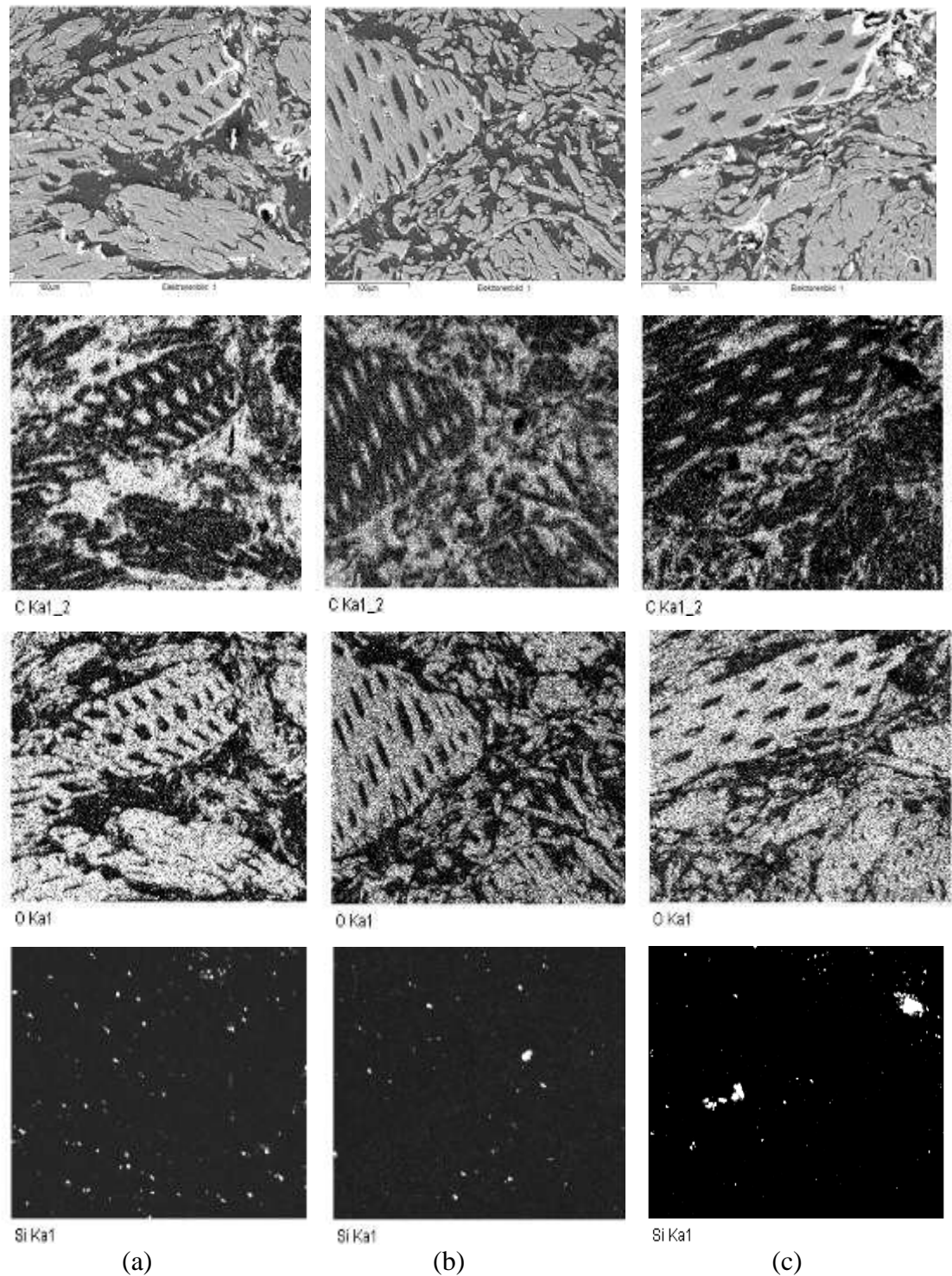


Figure 5.18: SEM-EDX of polished cross-section specimen of WF/PP 70/30 (a) without treatment, (b) with 1.75% very high molecular weight bifunctional triethoxy-vinyl PDMS with 0.1% DCP and (c) with 1.75% very high molecular weight bifunctional triethoxy-vinyl PDMS with 0.1% DCP

The distribution of C, O and Si from the fractured specimen can be seen in Figures 5.16 and 5.17. The C is representing PP plastic, the O is representing the wood while the Si is representing the PDMS and the white spot in the images show the presence of the compounds. We can only say that there are adhesions or wetting between the PP and wood while we cannot really identify the distribution of the Si element in both specimens. If we look at the C element in Figure 5.18, we can say that the PP are more distributed and well dispersed in the treated composites compared to the untreated composites but no significant difference is obvious between composites with and without DCP. However, the Si element appeared to be present in both treated and untreated composites. The presence of Si element in the untreated composites specimen is believed to originate from SiC powder used during polishing the cross section. Therefore it is expected that the Si from the coupling agent is not detectable because the 1.75% of PDMS is far too little and the Si element in the compound is far too low and under the limit of the detector.

5.8 Microscopic analysis of very high molecular weight bifunctional triethoxy-vinyl PDMS composites with 0.1% DCP stained specimens

Afterwards it was tried to see the difference of the composites by staining them to distinguish the wood and PP and look under the optical microscope. From the following 20 μm microtomed slices of waxed composites images (Figure 5.19) we can see the difference in the microstructure of the composites with and without DCP. The wood particle has been stained with toluidine blue while the PP remains clear. The sample with 0.1% DCP gives very well homogenous surfaces with good matrices-wood interaction while in the composites without DCP, we can see free spaces or voids and lacked of adhesion between wood and PP.

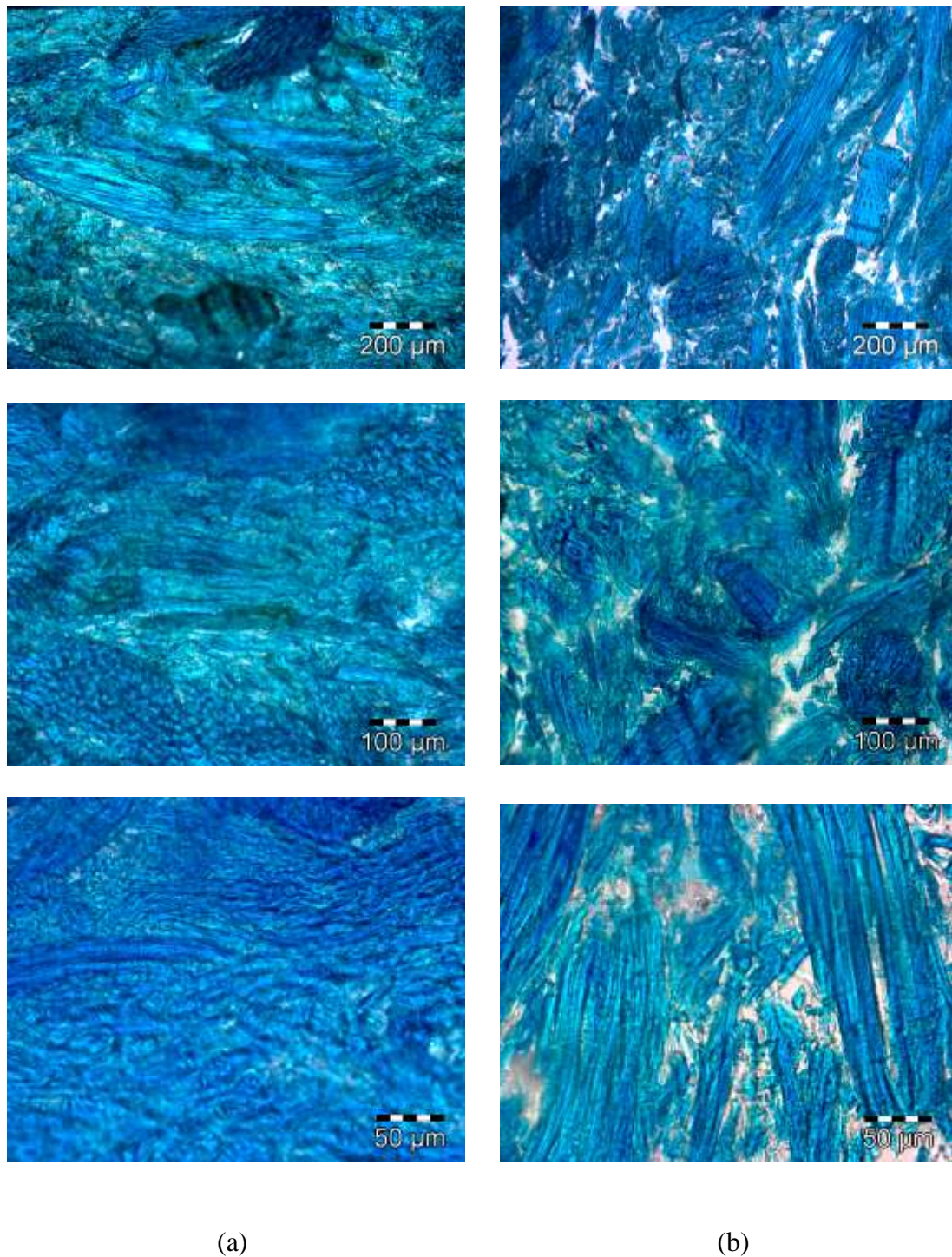


Figure 5.19: Microscopic images of WF/PP 70/30 composites treated with 1.75% very high molecular weight bifunctional triethoxy-vinyl PDMS. Different magnification images (a) With 0.1% DCP and (b) Without DCP.

5.9 Effect of DCP and very high molecular weight bifunctional triethoxy-vinyl PDMS treatment on water absorption

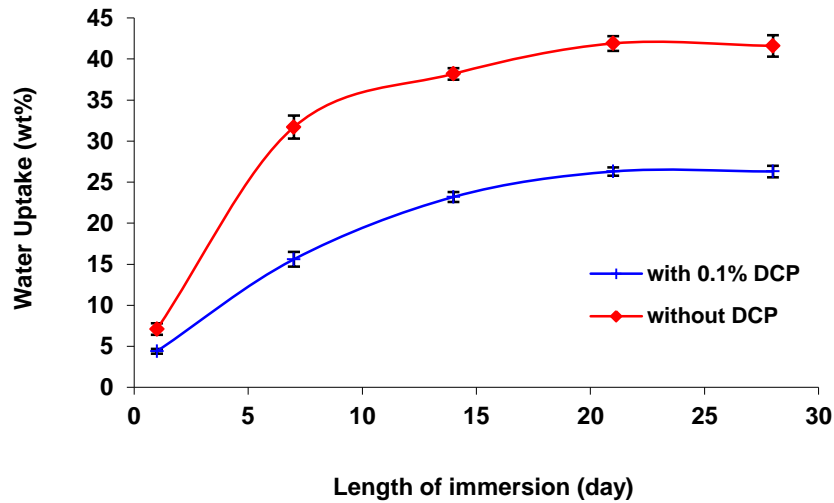


Figure 5.20: Influence of DCP on the water absorption of 70/30 WF/PP composites treated with 1.75% very high molecular weight bifunctional triethoxy-vinyl PDMS

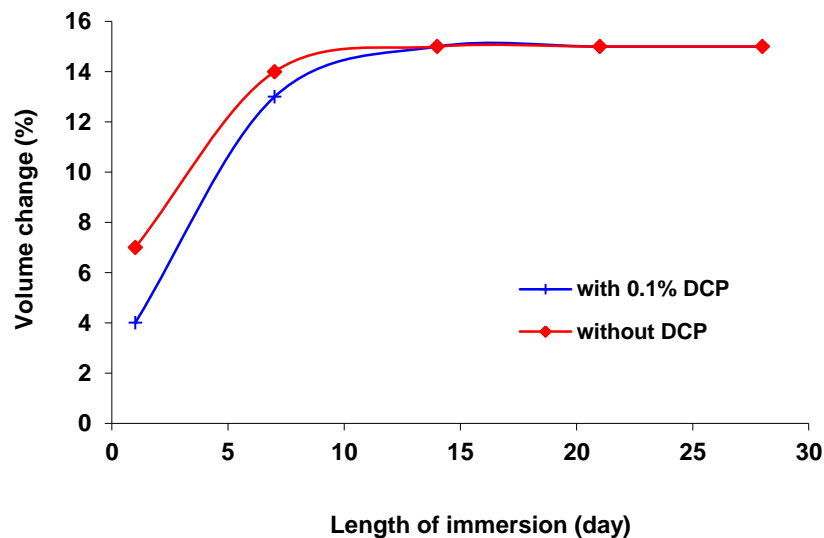


Figure 5.21: Influence of DCP on the volume of 70/30 WF/PP composites treated with 1.75% very high molecular weight bifunctional triethoxy-vinyl PDMS

The water absorption also gives better results with 1.75% very high molecular weight bifunctional triethoxy-vinyl PDMS treated composites processed with 0.1% DCP. Almost 45% lower water uptake was observed after 28 days of immersion. These results support the assumption that better interface has existed in the composites when DCP was used during processing.

5.10 DMA analysis of very high molecular weight bifunctional triethoxy-vinyl PDMS treated composite with 0.1% DCP

The shift in glass transition temperature of the composites with 0.1% DCP and increases of storage modulus which shows the amount of energy stored in the composite can be seen in Figure 5.22. As shown in the introduction section 2.5, the storage modulus tells us how much of the energy required to deform the sample is elastically recoverable (Chartoff *et al.*, 2009). The higher the storage modulus, the stiffer the composite is.

From the result, it can also be seen that the use of 0.1% DCP with 1.75% very high molecular weight bifunctional triethoxy-vinyl PDMS treatment has produced stiffer composites. However, T_g has shifted to a lower temperature. PDMS backbone is a very flexible polymer. The more flexible the backbone chain is, the easier the movement of the polymer, thus lowering the T_g . The PDMS backbone is so flexible that it has a T_g of -123 °C (Nielsen & Landel, 1994). Furthermore, as discussed in Chapter 5, DCP has caused chain scission in PP that also lowered the T_g . We can also see another transition starting around 45 °C with a very broad peak around 70 °C in the loss modulus of treated composite with 0.1% DCP. That might come from the excessed or unreacted DCP because the melting point for DCP is around 35 to 45 °C. This is because of very short retention time during processing that was only 30 seconds.

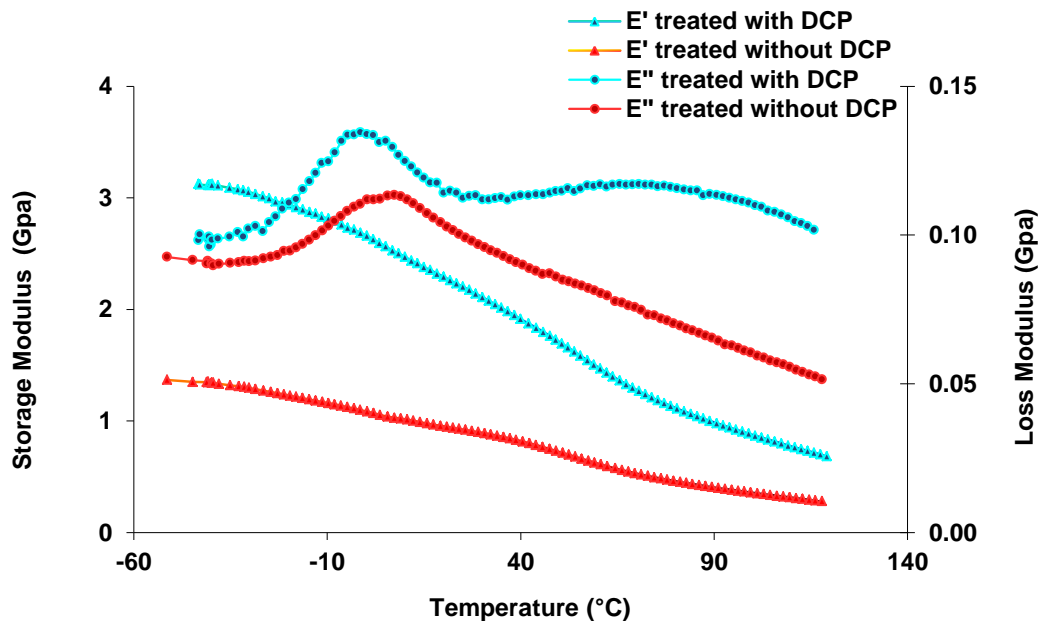


Figure 5.22: Storage modulus and loss modulus comparison of 70/30 WF/PP composites containing 1.75% very high molecular weight bifunctional triethoxy-vinyl PDMS with and without 0.1% DCP.

The activation energy (E_a) for the glass transition relaxation has also been calculated using the rearrangement of Arrhenius equation (Equation 2.2) as shown in Chapter 2, section 2.5. From this equation, the E_a was calculated by figuring out the

maximum temperatures of the tan delta at the different frequency as shown in Figure 5.23 and give a straight line of $\ln f$ versus $1/T$ from the Arrhenius-plot of the composites as shown in Figure 5.26. E_a is calculated from the slope of the plotted line multiply to the gas constant. Figure 5.25 shows the different in tan delta peak of different composite formulations at one Hz of frequency.

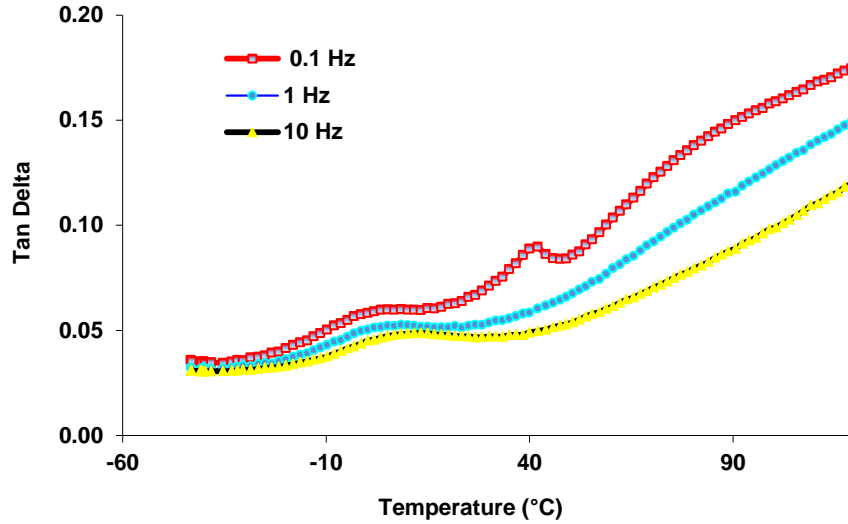


Figure 5.23: Tan delta peak of WF/PP 70/30 with 1.75% very high molecular weight bifunctional triethoxy-vinyl PDMS with 0.1% DCP at different frequency.

It has been reported that increasing of the test frequency or heating rate leads to a shift of T_g to a higher temperature (Chartoff *et al.* in Li *et al.*, 2000). From the above result (Figure 5.23), it can be seen that the increase of the T_g depends on the frequency. At a very low frequency that is 0.1 Hz a sharp transition peak around 40 °C can be seen. This is due to the crystalline loss peak of inter or intracrystalline motion origin of PP. This transition, also known as T_{α}^* , occur in semi crystalline polymers when the crystals slipped from their original origin. This transition only appeared with 1 Hz of frequency because at higher frequency the transition is shifted to a higher temperature. The same loss peak can be seen in the tan delta plot of the neat PP at the same 0.1 Hz frequency (Figure 5.24), which was also reported by Jarrigeon *et al.* (1980). Normally three transitions can occur in isotactic PP: the glass transition (T_g) could occur at a temperature range from -40 °C to 20 °C but commonly occur around 0 °C, α transition of crystalline part in PP (T_{α}^*) which also can occur in a very broad temperature ranging from around 40 °C to more than 100 °C and the melting (T_m) normally occur at 165 °C to 175 °C. (Jarrigeon *et al.*, 1980; Beck *et al.*, 1963; Patnaik, 2004).

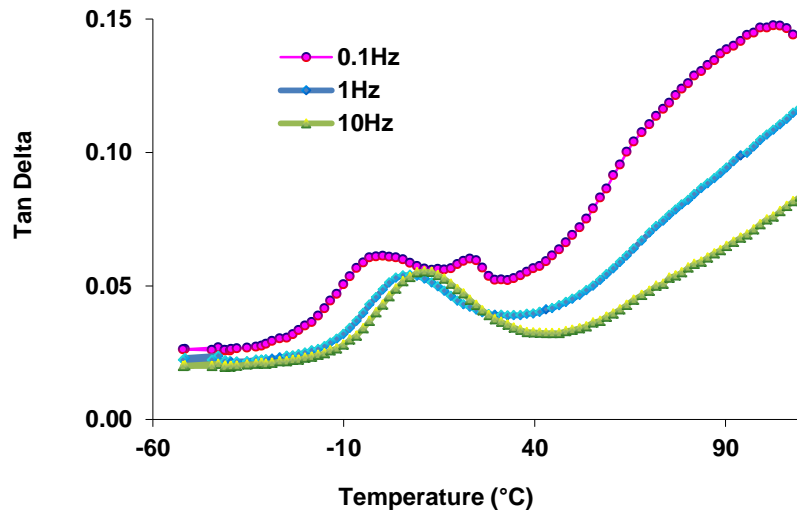


Figure 5.24: Loss peak in the PP tan delta plot at different frequency

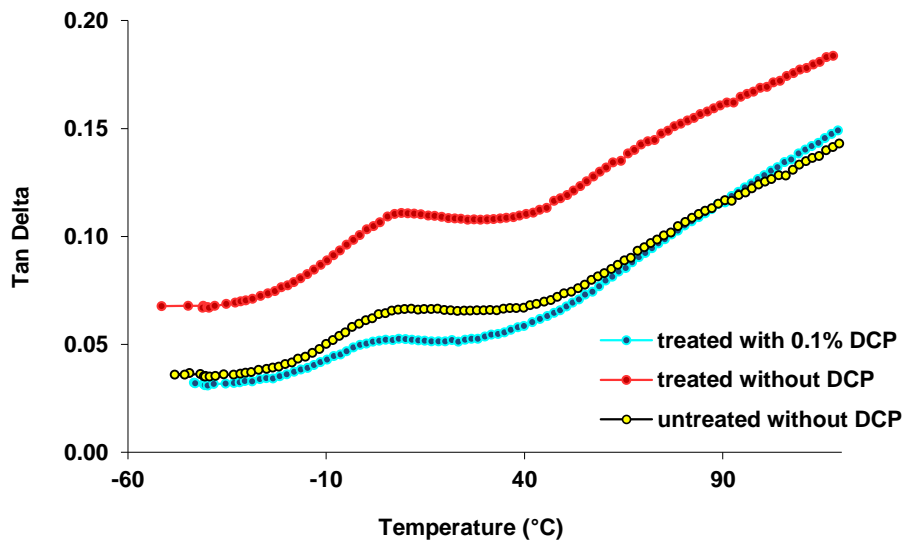


Figure 5.25: Tan delta peak comparison of WF/PP 70/30 with 1.75% very high molecular weight bifunctional triethoxy-vinyl PDMS with and without 0.1% DCP and untreated WF/PP 70/30 without DCP at 1Hz of frequency.

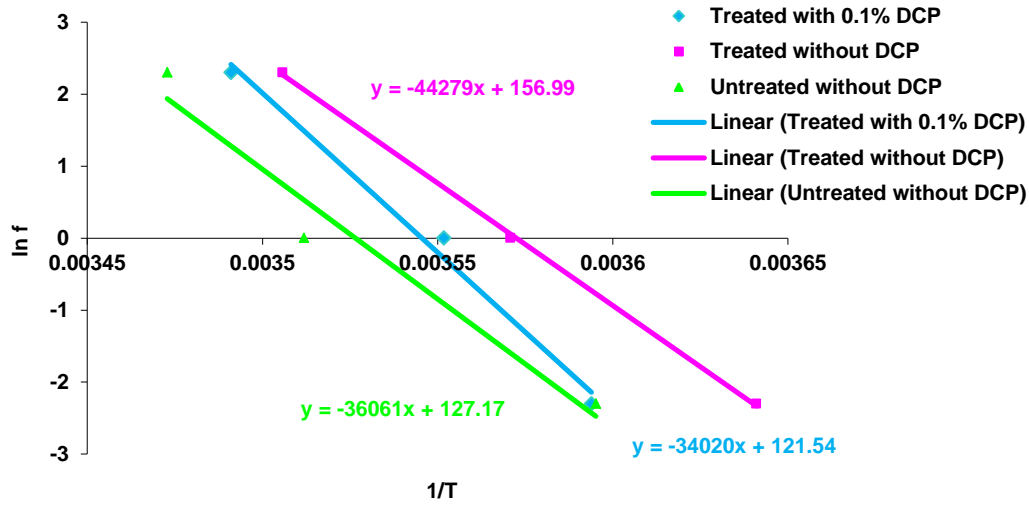


Figure 5.26: Arrhenius plot for 1.75% bifunctional triethoxy-vinyl PDMS treated composites with and without DCP and untreated composite without DCP.

E_a for the glass transition relaxation was taken from an average of at least three Arrhenius-plots. From the calculation, we found that the E_a of composites processed with 1.75% very high molecular weight bifunctional triethoxy-vinyl PDMS and 0.1% DCP has higher value, which is 371 ± 3 kJ/mol compared to the treated composites without DCP that is 281 ± 2 kJ/mol and untreated composites without DCP, 301 ± 1 kJ/mol. These results show that treatment containing 0.1% DCP gives better adhesion between wood and PP. Coupling reaction of PDMS might have bridged the wood and PP together and improved the strength. However it is believed that the flexibility of the PDMS backbone and the chain scission of PP caused by DCP have shifted the T_g to a lower temperature.

As the conclusion for this chapter it can be stated that 0.1% DCP is very effective in initiating the coupling reaction of the very high molecular weight bifunctional triethoxy-vinyl PDMS with wood and PP, resulting in better mechanical performance and adhesion than the treated composite without initiator. Further discussion of the very high molecular weight bifunctional triethoxy-vinyl PDMS treatment in the later chapter will be using 1.75% of the coupling agent as discussed earlier together with 0.1% DCP as the initiator.

6 Influence of coupling agent functional groups and molecular weights on the performance of WF/PP composites

Every functional group that is attached to a coupling agent has its own chemical behaviour and characteristic. When a coupling agent is used as an additive in a composites preparation, the aims of its reactions is to help providing better interphase between compounded matrix and the filler used. Several types of functionality, which potentially and theoretically will enhance the properties of WPC, have been chosen with our PDMS coupling agent. Through the following figures and discussions, we will see the potentiality and performance of the coupling agent in characterizing the properties of wood polypropylene composites. All formulations are using 0.1% DCP as initiator.

6.1 Mechanical properties for different functional groups PDMS

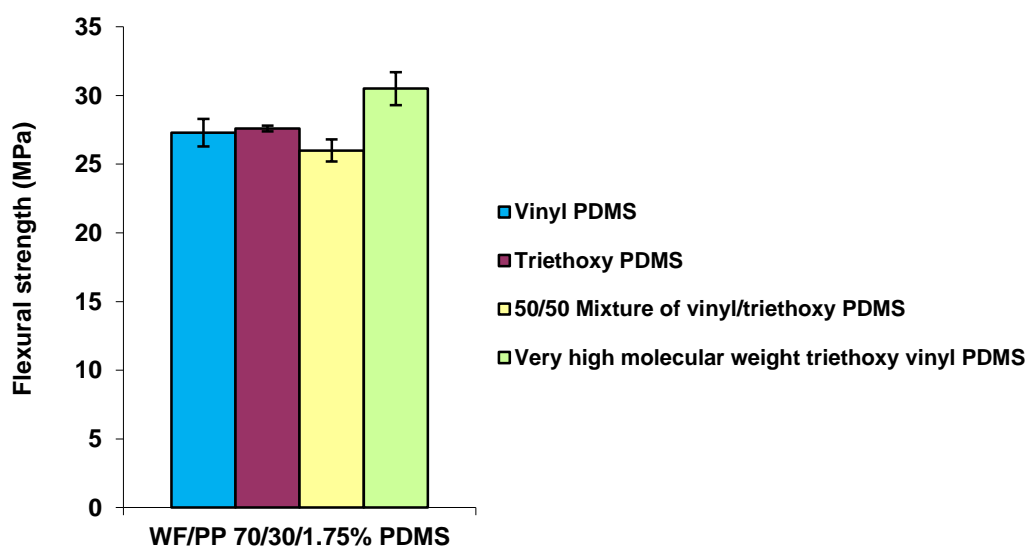


Figure 6.1: Flexural strength of 70/30 WF/PP treated with 1.75% PDMS containing different functional group and functional group attachment

As it can be seen from the Figure 6.1, the composite treated with very high molecular weight bifunctional triethoxy-vinyl PDMS has the highest value of flexural strength comparing to the composites treated with only single functional group attaching to the backbone. This is probably inducing by a better adhesion

occurring in the bifunctional PDMS treated composite where both functional groups may have chemically bond to the wood and PP providing a strong interface. An interphase between the wood and PP probably has bridged the component together hence enhancing the strength. Long chain of PDMS may as well entangle with PP or the cellulose chain, which can furthermore, give rise to the flexural strength. For the single functional group PDMS treated composites, chemical reaction may occur only on one end of the chain leaving the other chain free or just physically reacting with the wood or PP. Vinyl PDMS is expected to chemically bonding with PP and physically bonding with wood, while triethoxy PDMS is expected to chemically bonding to the wood during impregnation and may physically entangling with PP during processing. For the composite with 50/50 mixture of both vinyl and triethoxy PDMS, the vinyl part may chemically react to PP while the triethoxy part may chemically react to the wood and both vinyl and triethoxy PDMS may also physically entangle between them and also to wood and PP.

This is why we can see that the modulus of elasticity (Figure 6.2) is the highest for the composites with bifunctional PDMS, following by the mixture of both and the lowest for the single functionality. The modulus of elasticity of composites is not affected by the adhesion, unless the composites were strongly adhered together. The formation of strong interphase in the composites coupled with the bifunctional group has given the composites better stiffness compared to the others. The 50/50 mixture of vinyl/triethoxy treated composites is also stiffer than the single functional group may be due to the existence of more physical entanglement in the composites between the vinyl and triethoxy PDMS and between the wood and PP. These entanglements probably do not form strong interfaces, but their presence is enough to increase the stiffness.

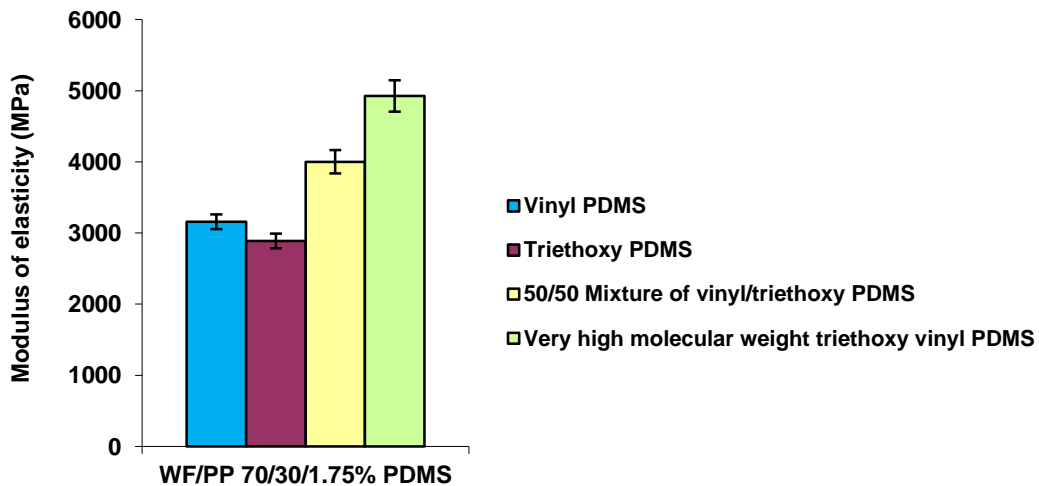


Figure 6.2: Modulus of elasticity of 70/30 WF/PP treated with 1.75% PDMS containing different functional group and functional group attachment

6.2 DMA analysis for different functional groups PDMS

The DMA results of composite treated with a 50/50 mixture of the single functional group PDMS show a slight higher transition in the glass transition temperature comparing to the bifunctional PDMS treated composite (Figures 6.3 and 6.4). The storage modulus is also higher for the mixture of single functional PDMS. DMA is measuring the viscoelastic properties of materials at the molecular level. The mobility of chain segments plays an important role in showing the results. A small difference in the freedom of chain movement will affect the transition of the materials. As discussed, the composite treated with the mixture of single functional PDMS is expected to have more chain entanglement between coupling agents, wood and PP chain. The higher T_g and storage modulus obtained with the composite treated with 50/50 mixture of single PDMS could be due to the entanglement phenomena. Thus, less segmental chain movements of the composite with the mixture of single functional PDMS comparing to the bifunctional PDMS. However, from the Arrhenius plot (Figure 6.5), the E_a of the glass transition has been calculated, and it can be seen that the E_a for composite containing bifunctionality PDMS is higher, which is 371 ± 3 kJ/mol compared to the mixture that is only 269 ± 1 kJ/mol. This shows that the interphase bonding in the bifunctional PDMS treated composites is stronger than the interphase bonding in the mixture of the single functional PDMS.

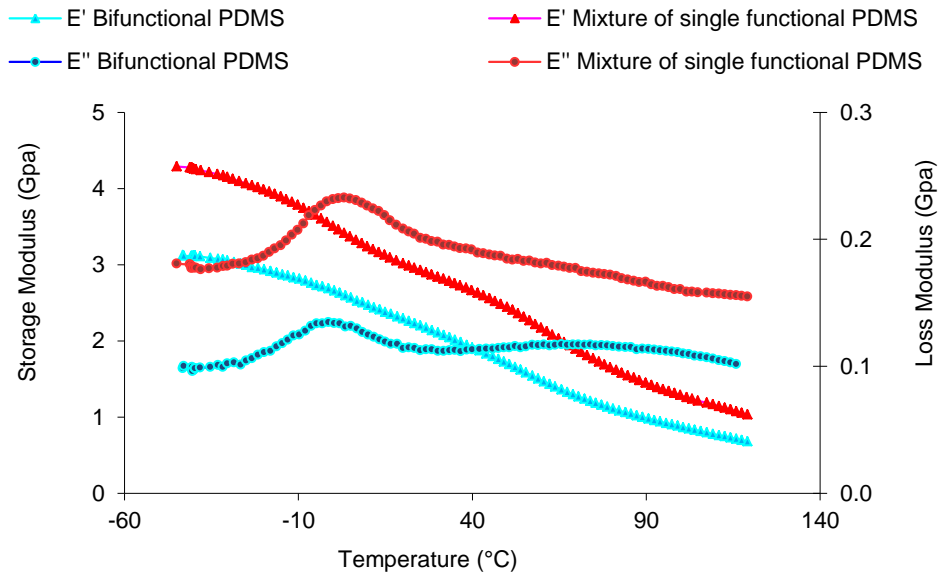


Figure 6.3: Storage modulus and loss modulus comparison of 70/30 WF/PP composites containing 1.75% treatment of very high molecular weight bifunctional triethoxy-vinyl PDMS and 50/50 mixture of triethoxy PDMS/vinyl PDMS.

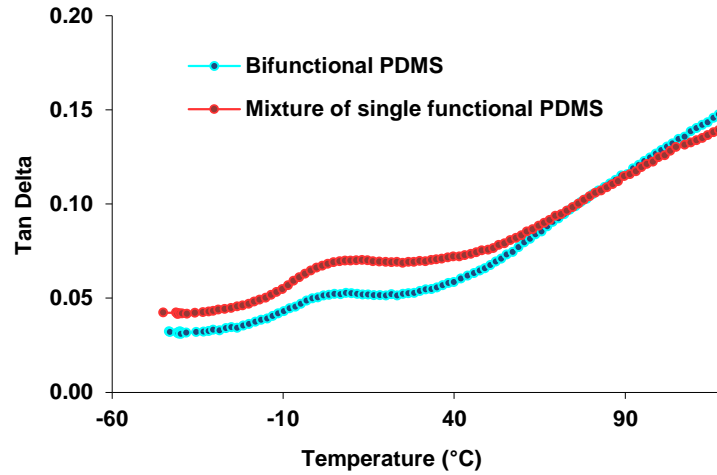


Figure 6.4: Tan delta peak comparison of 70/30 WF/PP composites containing 1.75% treatment of very high molecular weight bifunctional triethoxy-vinyl PDMS and 50/50 mixture of triethoxy PDMS/vinyl PDMS at 1Hz of frequency.

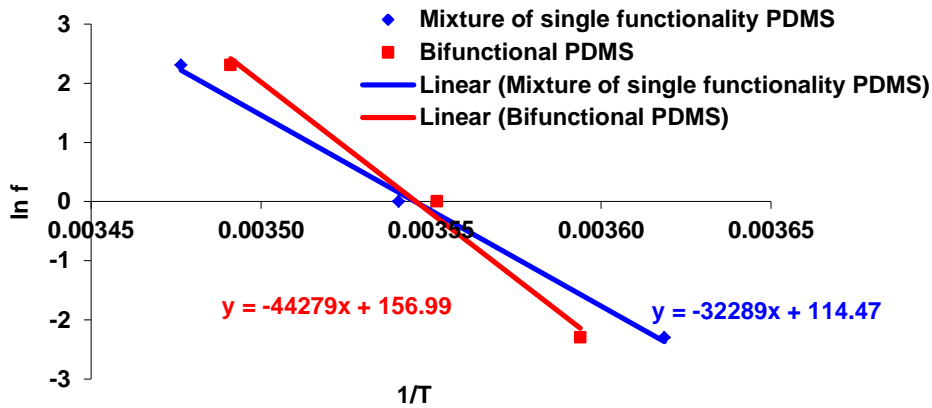


Figure 6.5: Arrhenius plot of the tan delta peak for the comparison of 50/50 mixture of triethoxy PDMS/vinyl PDMS and very high molecular weight bifunctional triethoxy-vinyl PDMS.

From these results it can be stated that several adhesion reactions might have taken place during processing the 70/30 WF/PP composites containing bifunctional PDMS:

- Covalent bonding (C-O) through condensation from the reaction between triethoxy group in PDMS and the cellulose hydroxyl group in wood,
- Covalent bonding (C-C) through radical reaction between vinyl group in PDMS and the PP chain,
- Secondary interaction through hydrogen bonding of OH cellulose and OH from hydrolysis of triethoxy group from the bifunctional PDMS,
- van der Waals interaction between the free chain segment in the composites and
- Entanglements of long PDMS (Si-O-Si) chain with the PP chain.

The following reaction mechanisms (Figures 6.6 and 6.7) might represent the reactions occurred in the composites.

6.3 Reaction mechanisms of WF/PP composites treated with bifunctional triethoxy-vinyl PDMS

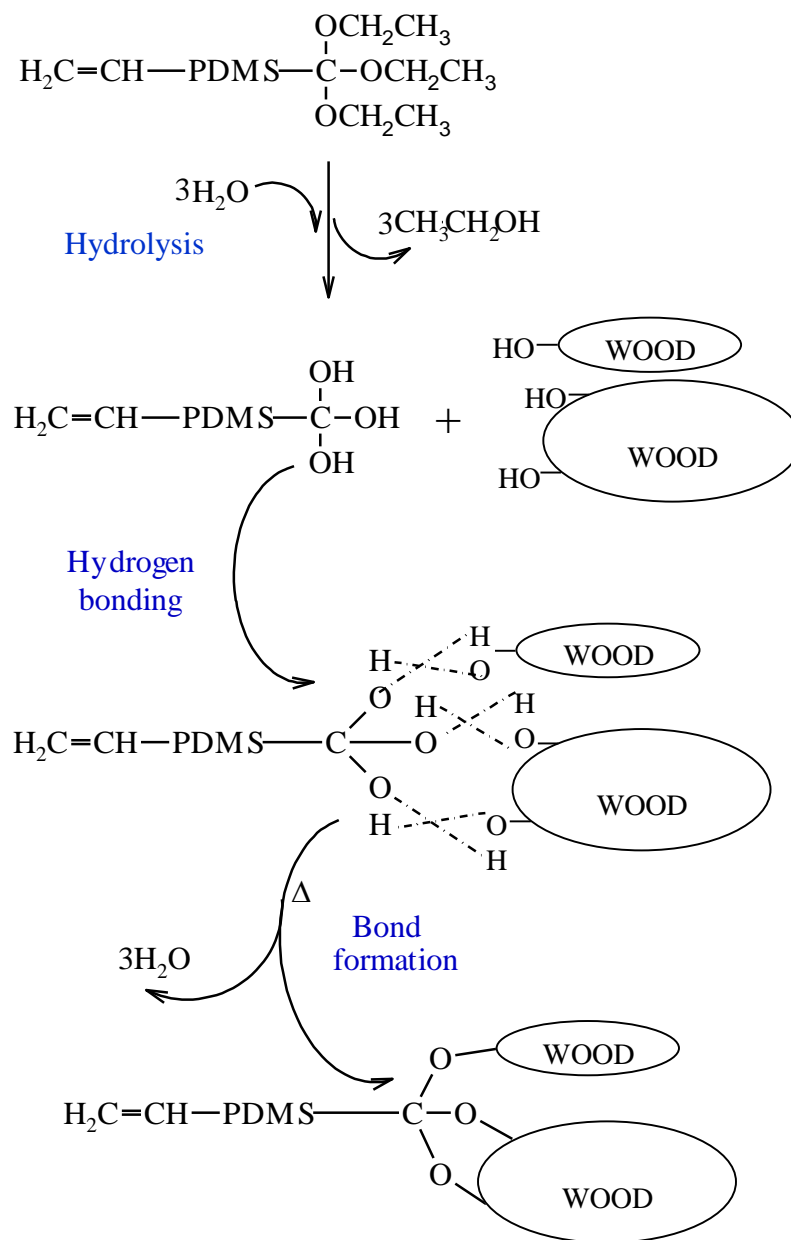


Figure 6.6: Expected reaction mechanisms between wood and bifunctional triethoxy-vinyl PDMS during impregnation.

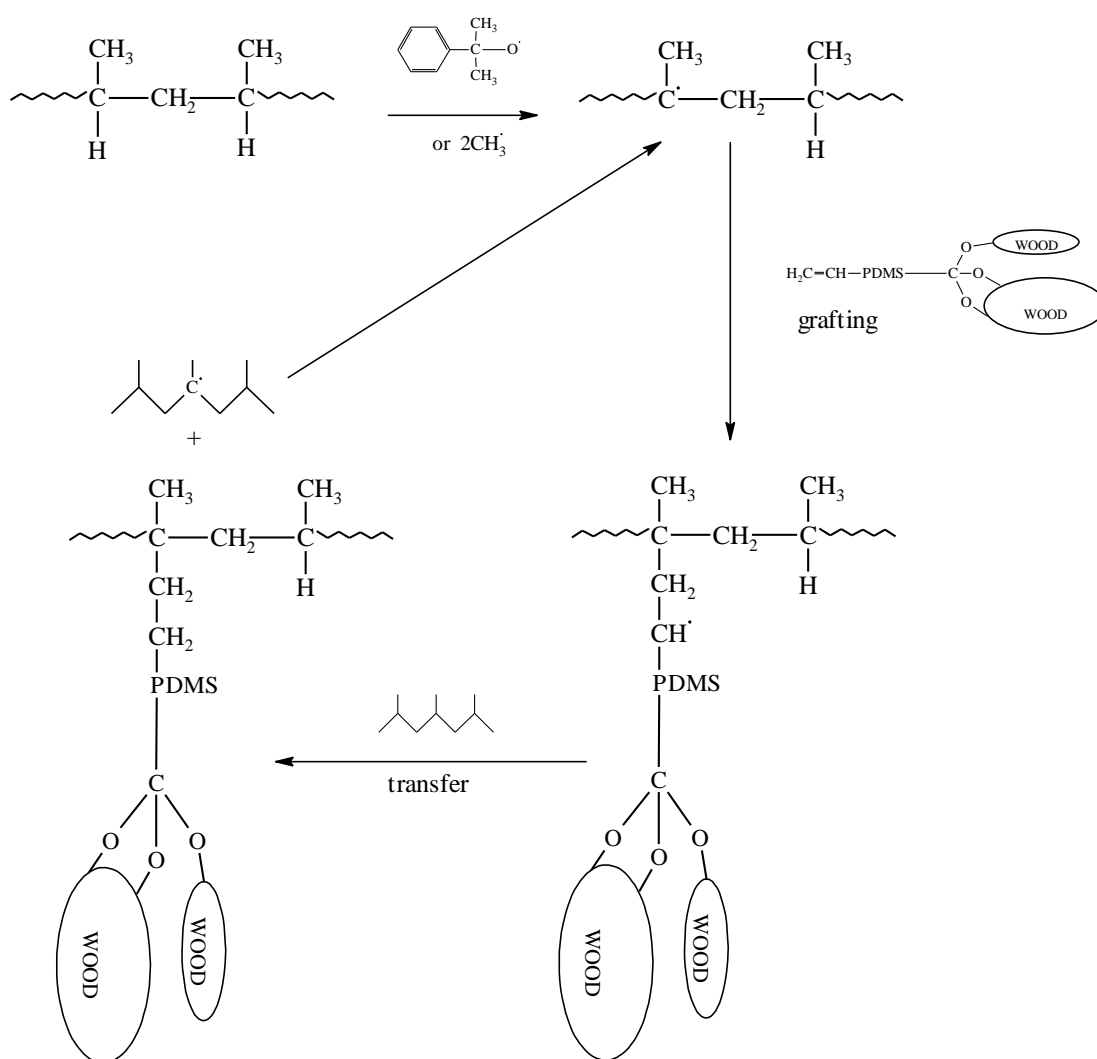


Figure 6.7: Expected reaction mechanisms between bifunctional triethoxy-vinyl PDMS and PP chain during compounding.

6.4 ATR-FTIR analysis of WF/PP composites treated with bifunctional triethoxy-vinyl PDMS

Further investigation has been made to confirm the covalent bonding through ATR-FTIR with the treated wood sample after impregnation. C-O-C bonding is expected to exist at wavelength 1070 – 1150 cm⁻¹ (Figure 6.8). To ensure the result, soxhlet extraction has been done to the 1.75% PDMS treated wood while the untreated wood was extracted as standard. Both extractions were done with xylene for 24 hours. After that, another FTIR analyses was run with the extracted wood. However, the results do not confirm the existence of bonding as the dissolved wood flours of both treated and untreated samples give the same spectra (Figure 6.9).

Perhaps the existence of new C-O-C bonding is overlapping with the existing C-O-C bonding in wood.

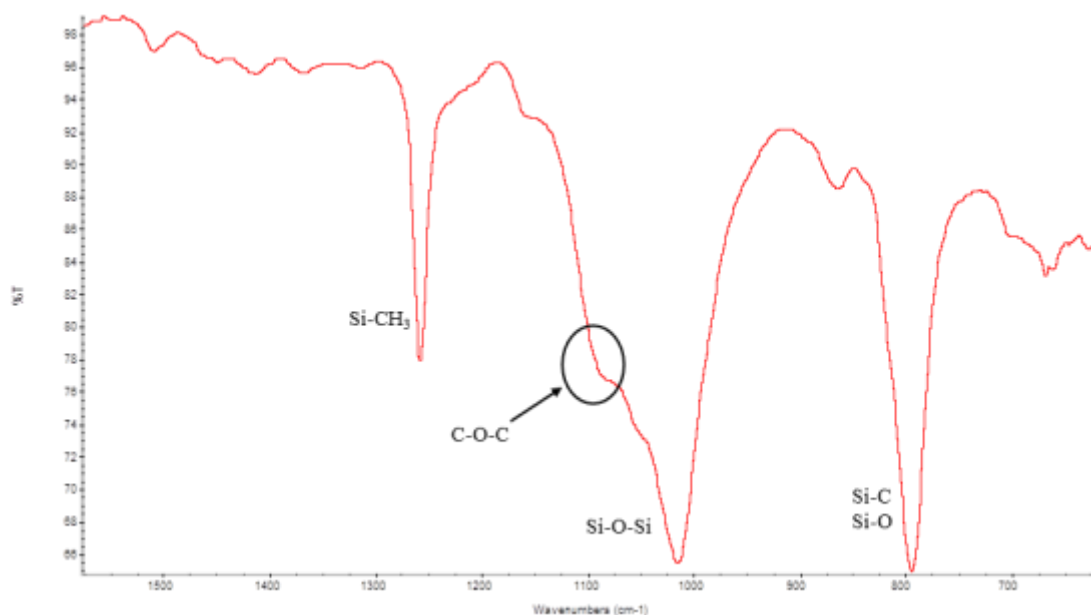


Figure 6.8: Expected C-O-C Bonding ($1070 - 1150 \text{ cm}^{-1}$) from ATR-FTIR spectrum of 1.75% very high molecular weight bifunctional triethoxy-vinyl PDMS treated wood flour.

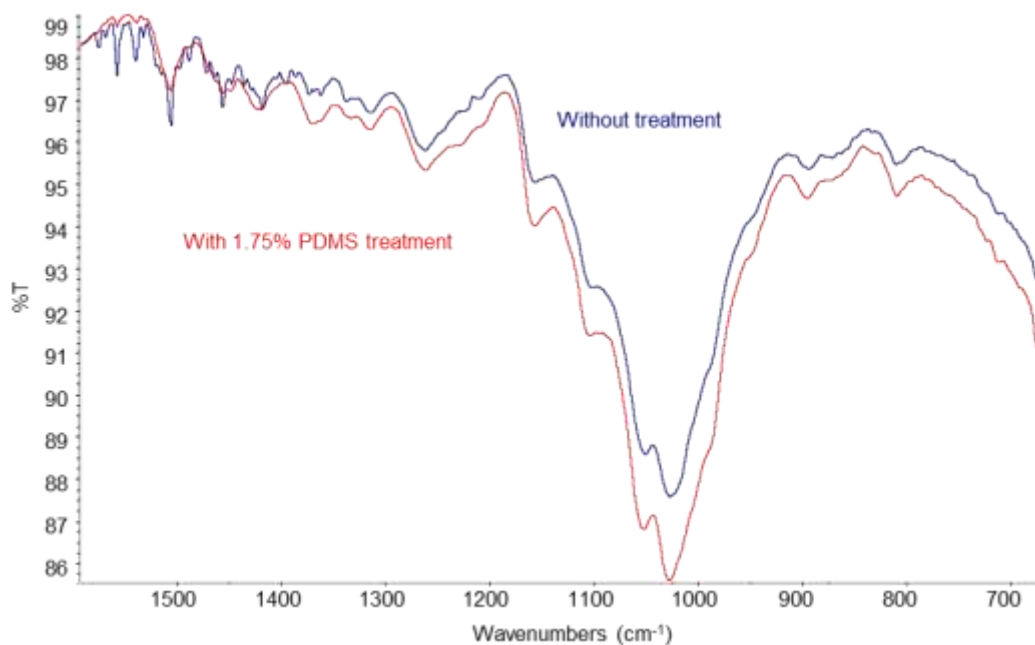


Figure 6.9: Comparison of 1.75% very high molecular weight bifunctional triethoxy-vinyl PDMS treated and untreated wood flour after 24-hour xylene extraction. No new C-O-C bonding ($1070 - 1150 \text{ cm}^{-1}$) exists; both treated and untreated wood flour showing the same spectrum.

6.5 Microscopic images of WF/PP composites treated with bifunctional triethoxy-vinyl PDMS

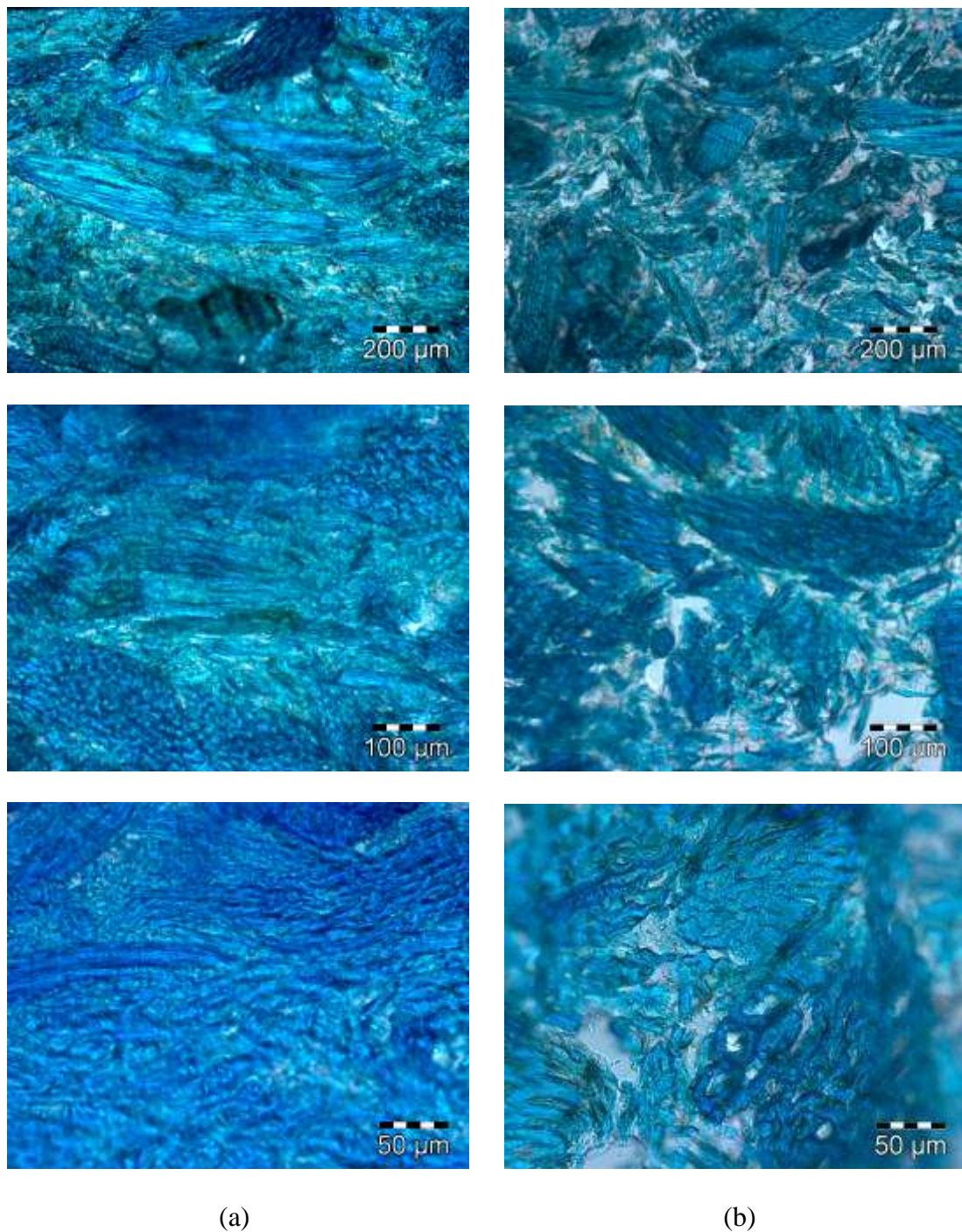


Figure 6.10: Microscopic images of 70/30 WF/PP composites (a) treated with 1.75% very high molecular weight bifunctional triethoxy-vinyl PDMS and (b) without treatment at different magnification.

Even though the type of chemical bonding existing in the composite treated with the very high molecular weight bifunctional triethoxy-vinyl PDMS cannot be proven, the microscopic images show that the coupling agent works very well and produces much better interaction between the phases. Composites void is hardly found in the treated composites compared to the images of the untreated composites, where the adhesion between wood and plastic is very poor. A lot of voids or empty spot are recognizable in between the untreated composites. These images supported that the bifunctional coupling agent really reacted at the interface of wood and PP.

6.6 Influence of different molecular weight bifunctional triethoxy-vinyl PDMS on WF/PP composites performance

There were three different molecular weight of bifunctional PDMS used: the low molecular weight, high molecular weight and the very high molecular weight bifunctional triethoxy-vinyl PDMS. From Figure 6.11, it can be seen that by adding 1.75% bifunctional triethoxy-vinyl PDMS coupling agent to the 70/30 WF/PP composites the flexural strength has increased. The very high molecular weight bifunctional PDMS gives the highest flexural strength as compared to the lower molecular weight. However, when the same amount of these coupling agents is used in the composites containing 70% plastic, no positive effect was observed on the flexural strength (Figure 6.12). These results show that the bifunctional PDMS reacted better with the wood phase.

As discussed earlier, the drawback from the chain scission reaction caused by DCP on the PP has defeated the benefit of the reaction occurred in the system when 70% plastic were used in the composites. More plastic caused more chain scission and the lower content of wood, that is 30%, is much too low to affect the flexural strength when reacted and coupled. 30% of wood will probably react with 30% of PP and the 40% unreacted PP will possibly go through the chain scission. This will give more influence in lowering the flexural strength affected by coupling reaction being defeated by the chain scission. This result also shows that every system needs its own recipe and formulation. 70% plastic may probably need less amount of DCP for the coupling reaction although further investigation will be needed.

The very high molecular weight bifunctional PDMS used with 70/30 WF/PP gives the highest flexural strength compared to the lower molecular weight. Better interaction existed when longer chain length PDMS was used. There will be more molecular entanglement from the longer mobile chain. This also will give rise to the secondary van der Waals interaction, which will also enhance the performance. The difference between low molecular weight and high molecular weight PDMS is just within the error limit and not significant to be compared.

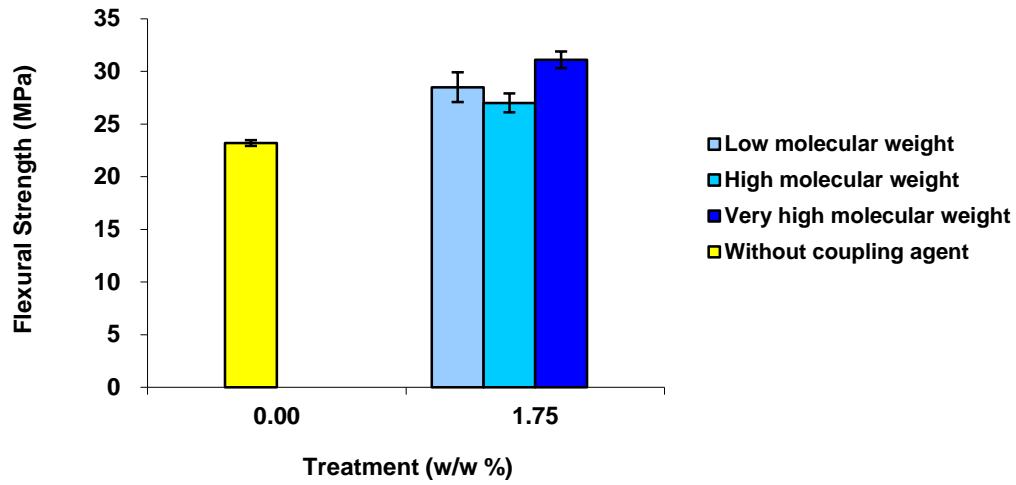


Figure 6.11: Influence of bifunctional triethoxy-vinyl PDMS molecular weight on flexural strength WF/PP 70/30

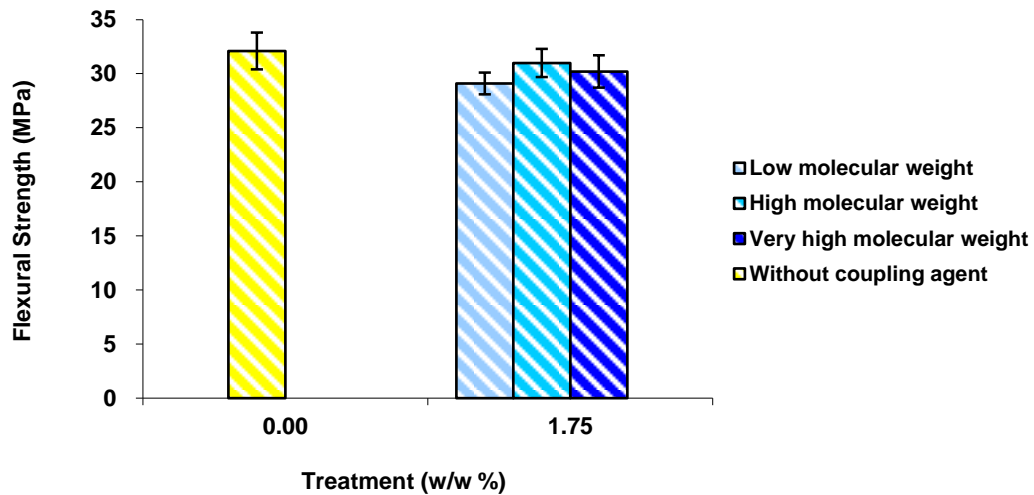


Figure 6.12: Flexural strength of WF/PP 30/70 treated with difference molecular weight bifunctional triethoxy-vinyl PDMS

The modulus of elasticity increased with the addition of 1.75% bifunctional PDMS in 70/30 WF/PP composites (Figure 6.13) but no significant improvement was observed when 70% PP (Figure 6.14) was used in the composites. The very high molecular weight gives the highest modulus of elasticity, as discussed earlier, due to strong adhesion existing in the composites. The impact strength also shows a better interaction existing in the composites containing more wood and the very high molecular weight bifunctional PDMS, as well shows the highest value compared to the lower molecular weight (Figures 6.15 – 6.16).

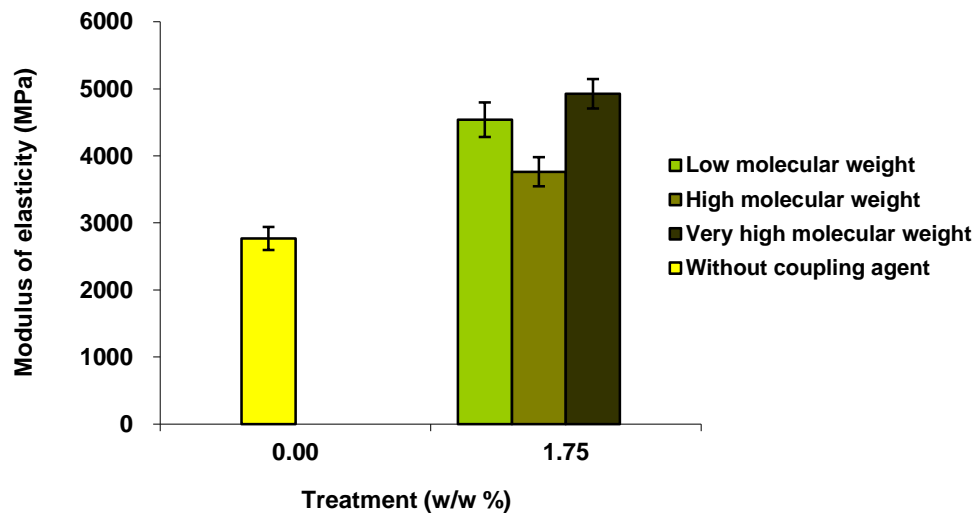


Figure 6.13: Influence of bifunctional triethoxy-vinyl PDMS molecular weight on modulus of elasticity WF/PP 70/30

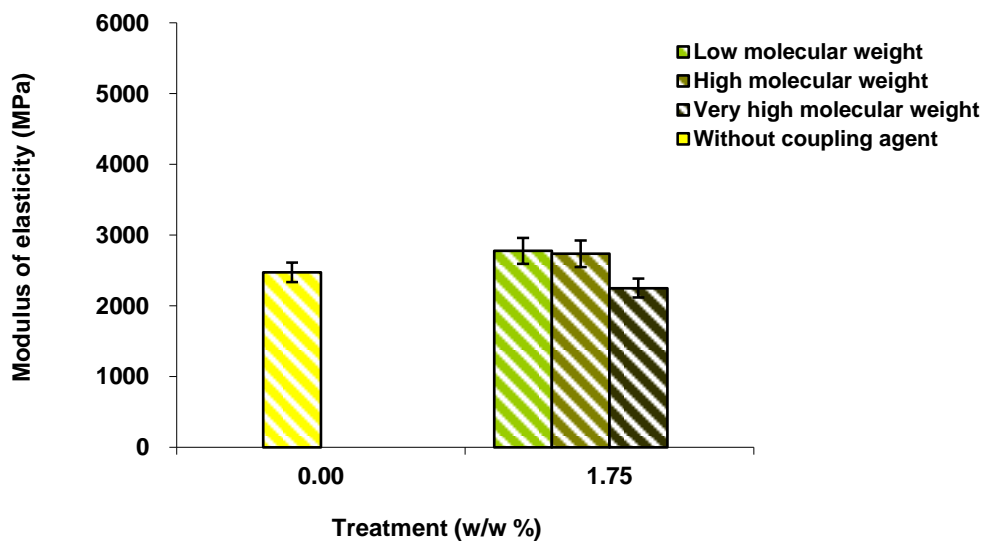


Figure 6.14: Modulus of elasticity of WF/PP 30/70 treated with difference molecular weight bifunctional triethoxy-vinyl PDMS

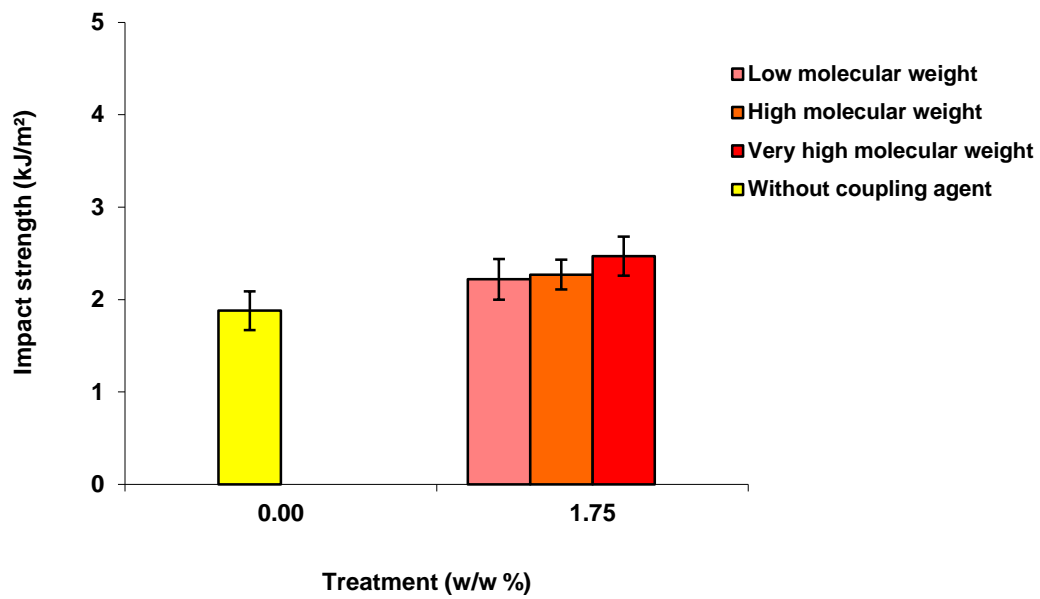


Figure 6.15: Influence of bifunctional triethoxy-vinyl PDMS molecular weight on impact strength WF/PP 70/30

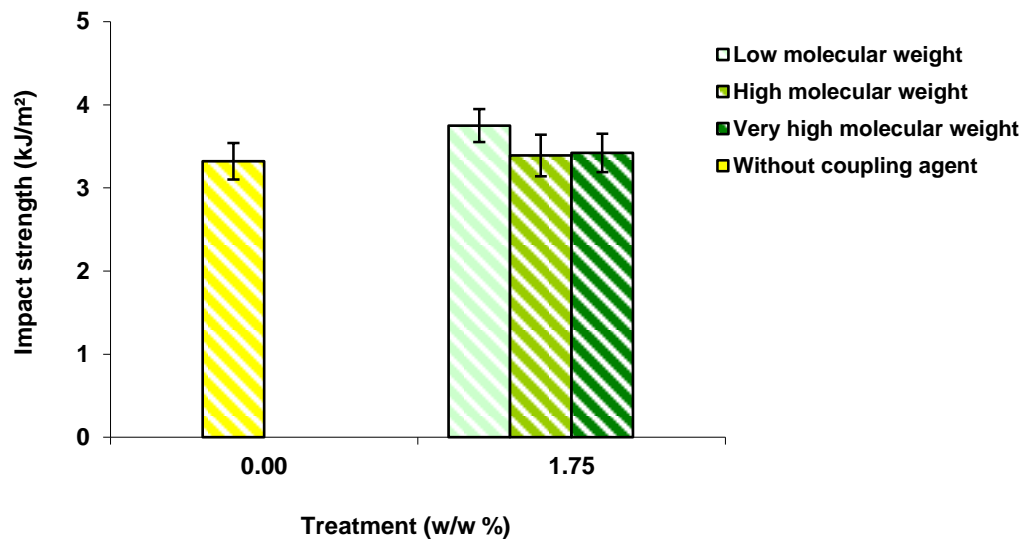


Figure 6.16: Impact strength of WF/PP 30/70 treated with difference molecular weight bifunctional triethoxy-vinyl PDMS

7 Very high molecular weight bifunctional triethoxy-vinyl PDMS coupling agent performance comparisons with industrially established MAPP

The previous results have demonstrated the performance and characteristic of the wood/polypropylene coupled by very high molecular weight bifunctional triethoxy-vinyl PDMS. In Chapters 5 and 6 we have discussed and proved that this new coupling agent can successfully enhance the properties of WPC produced comparing to the neat WPC. However, it cannot be concluded how far the improvements have achieved, if we do not standardize and compare them with something widely been used in industry. In this chapter, we intend to compare the mechanical properties and performance of our WPC with WPC containing industrial MAPP that is Licocene PP MA 6252 from Clariant GmbH, Gersthofen, Germany. MAPP has vastly been used in the wood plastic industry, and it is well known to perform effectively (Ichazo *et al.*, 2001; Acha *et al.*, 2007).

The WPCs containing MAPP coupling agent that are used for the comparison in this research were produced by the same processing method as producing WPC containing PDMS coupling agent described in Chapter 3 sections 3.3. All the samples for testing were prepared and tested the same way as with the very high molecular weight bifunctional triethoxy-vinyl PDMS composites. The following figures show the results.

7.1 Mechanical properties

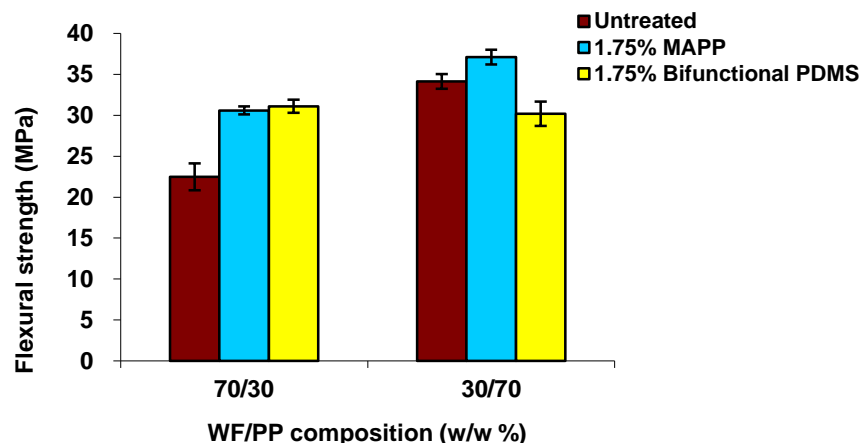


Figure 7.1: Flexural strength performance comparison of coupling agent with different composition

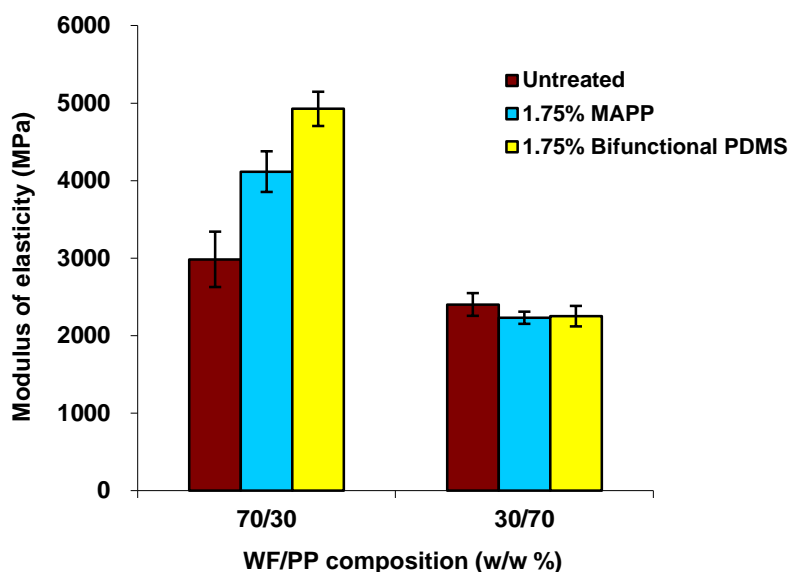


Figure 7.2: Modulus of elasticity performance comparison of coupling agent with different composition

Table 7.1: Average composites density for flexural test

Coupling agent	Density (WF/PP) (g/cm ³)			
	70/30		30/70	
	Mean	SD	Mean	SD
Without	1.14	0.01	0.96	0.05
MAPP	1.16	0.07	0.97	0.08
Bifunctional PDMS	1.18	0.02	0.96	0.07

As it can be seen the flexural strength of 70/30 WF/PP composites containing either MAPP or PDMS coupling agents are more or less the same but higher than the composites without a coupling agent (Figure 7.1). Though, the flexural strength of composites containing more plastic (30/70 WF/PP) decreased for PDMS coupling agent and a bit increased for MAPP. That is because MAPP has better interaction with PP. Theoretically the strength of reinforced PP increases with the increasing filler loading up to an optimum amount. After that, further increment of filler will only decrease the strength. The decrement is normally because of too much fillers and lack of adhesion or wetting. From the 30/70 WF/PP composite result, the same phenomenon is obvious. MAPP coupling agent works better with PP than wood and the optimum filler loading with the influence of MAPP coupling agent might be around 30% while the PDMS coupling agent which works much more better with wood than PP might not influence the adhesion reaction between wood and PP,

giving lower optimum filler loading, which is why the value is lower than the composites without a coupling agent.

The modulus of elasticity (Figure 7.2) of the composite treated with PDMS is better than when 70% of wood was used, which is a normal phenomenon of a filled plastic. No significant difference can be seen with 70% PP composites.

The results in Table 7.1 demonstrate that densities of the composites containing the same composition of WF/PP with the different coupling agent are comparable. Density of every tested sample also affects the result of mechanical testing. The density of the composites does not vary so much between one another in the same composition because they were pressed with a specific amount in a same size of the frame with a similar hot press condition.

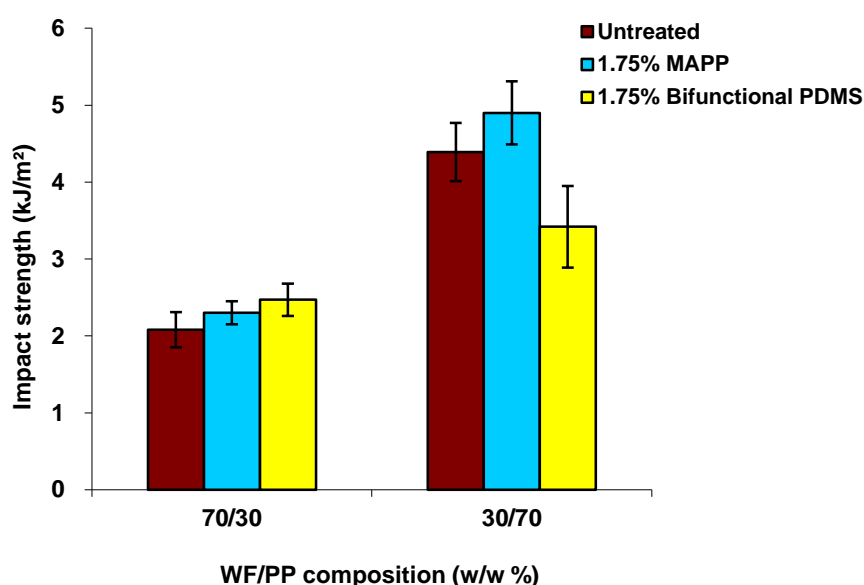


Figure 7.3: Impact strength performance comparison of coupling agent with different composition

The impact strength (Figure 7.3) is not so significant to be discussed because the results are within the error bars showing that impact strength is more affected by the PP composition than by treatment.

7.2 Microscopic images

From Figure 7.4 we can see the microscopic images of both coupling agents treated composites with 70/30 composition at the different magnification. Both composites show comparable images with very good wood and PP interaction. Both coupling agents have very homogenous surfaces and composite void is hardly found.

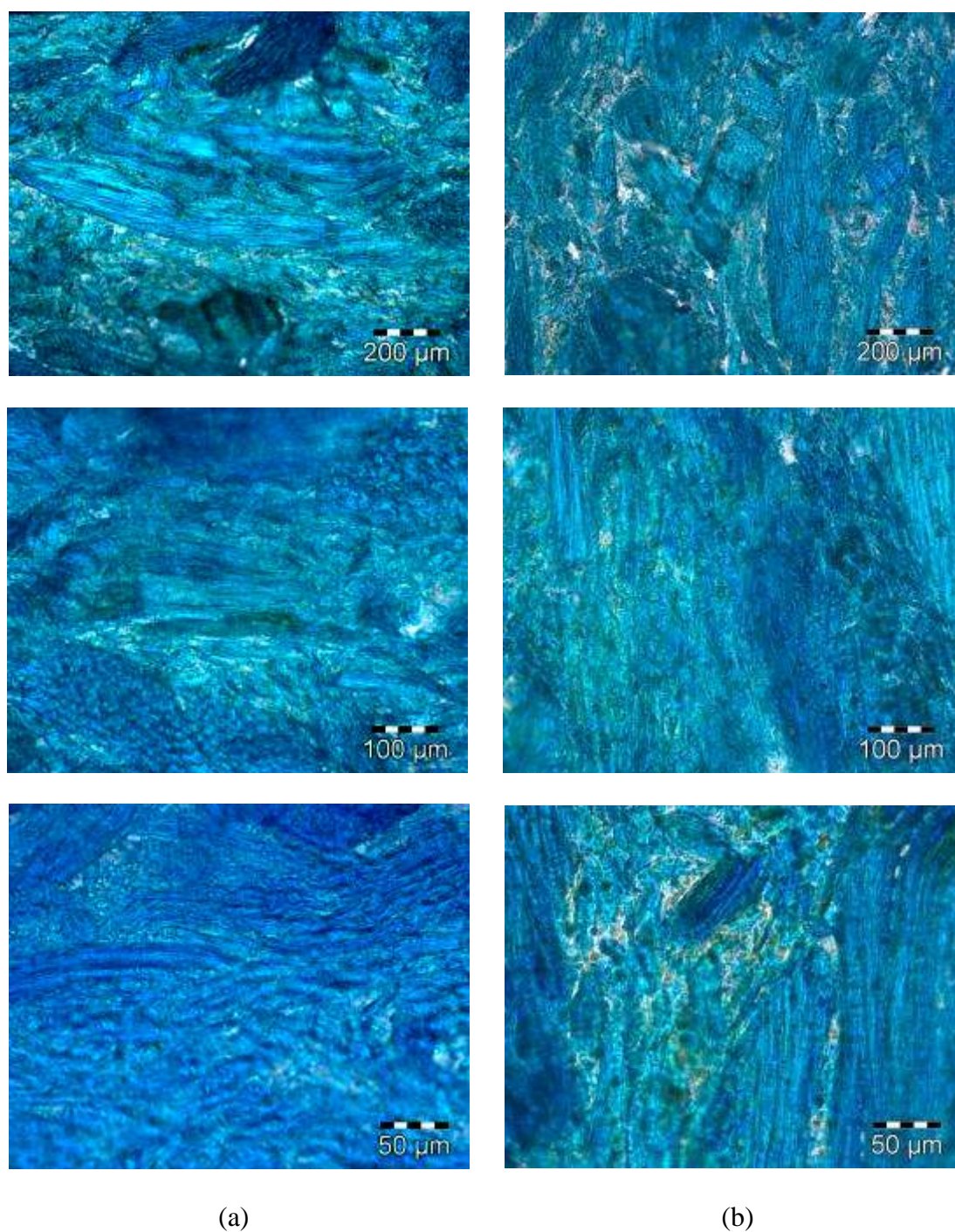


Figure 7.4: Microscopic images of 70/30 WF/PP composites (a) treated with 1.75% very high molecular weight bifunctional triethoxy-vinyl PDMS and (b) 1.75% MAPP at different magnification.

7.3 DMA analysis

As shown by the mechanical properties and microscopic images, both MAPP and PDMS treated composites are comparable and their performances are more or less within the same level. Further analysis to the molecular level confirms these results. The very high molecular weight bifunctional triethoxy-vinyl PDMS results is more or less a copy of each other storage modulus (Figure 7.5) and tan delta peaks (Figure 7.6), where just a slightly lower glass transition could be seen comparing to the MAPP.

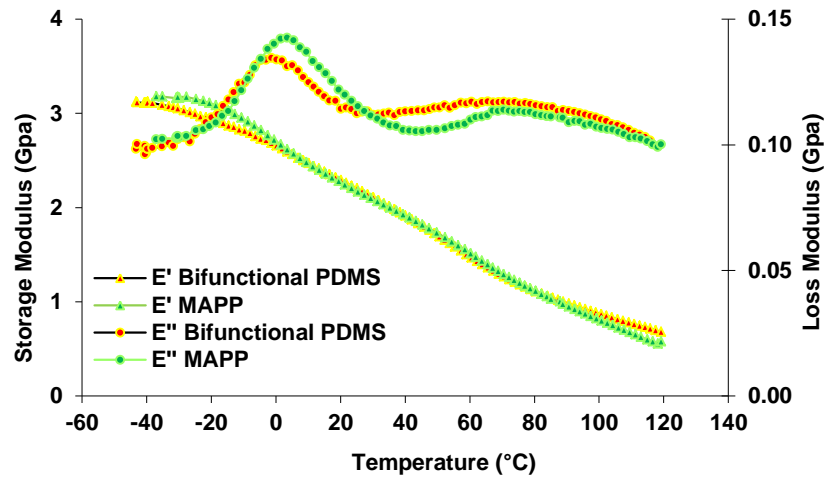


Figure 7.5: Storage modulus and loss modulus comparison of 70/30 WF/PP composites containing 1.75% treatment of very high molecular weight bifunctional triethoxy-vinyl PDMS and 1.75% MAPP.

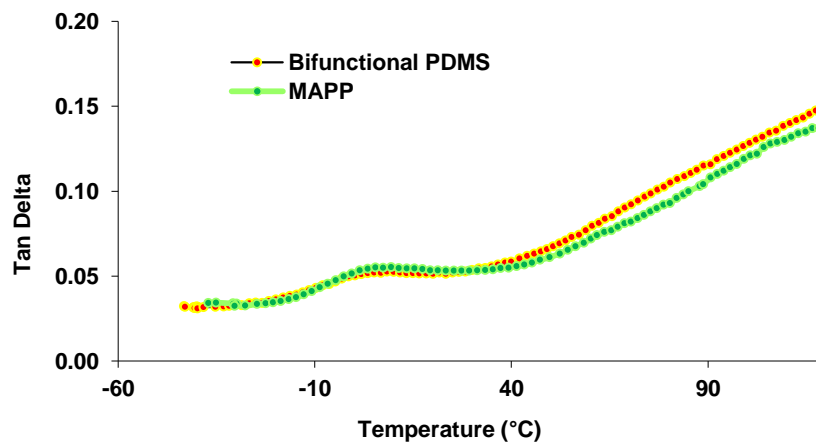


Figure 7.6: Tan delta peak comparison of 70/30 WF/PP composites containing 1.75% very high molecular weight bifunctional triethoxy-vinyl PDMS and 1.75% MAPP at 1 Hz of frequency.

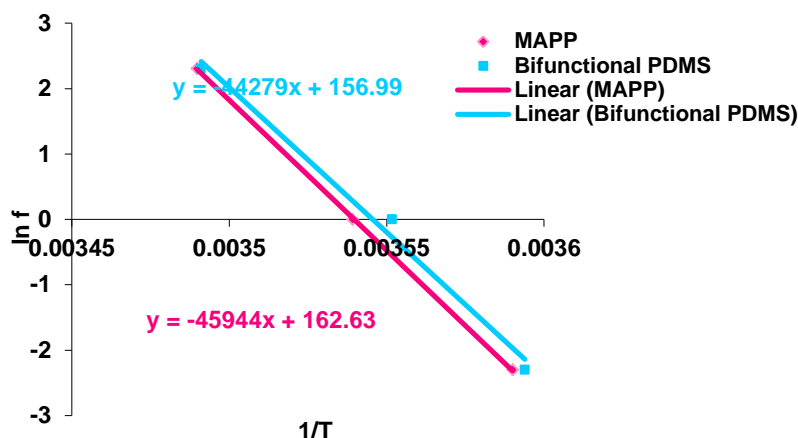


Figure 7.7: Arrhenius Plot of 70/30 WF/PP composites treated with bifunctional PDMS and MAPP

Arrhenius plot has also been made and the E_a of the glass transition for both bifunctional PDMS and MAPP treatments has been compared (Figure 7.7). The results show that composites treated with MAPP have a bit higher E_a , which is 382 ± 1 kJ/mol compared to the bifunctional PDMS, which is 371 ± 3 kJ/mol. This is probably due to better interaction between the MAPP and PP compared to bifunctional PDMS and the shorter PP chain caused by chain scission when DCP was used. Shorter chain will less entangle and be easier to move. However, a 3% higher of the MAPP E_a value compared to the bifunctional PDMS E_a value is not a big difference and should be considered as comparable.

7.4 Water absorption

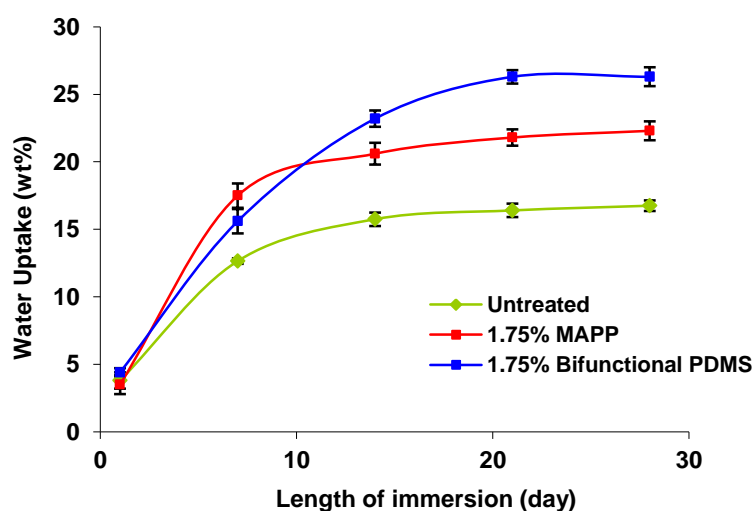


Figure 7.8: The effect of coupling agent on the water absorption of 70/30 WF/PP composites

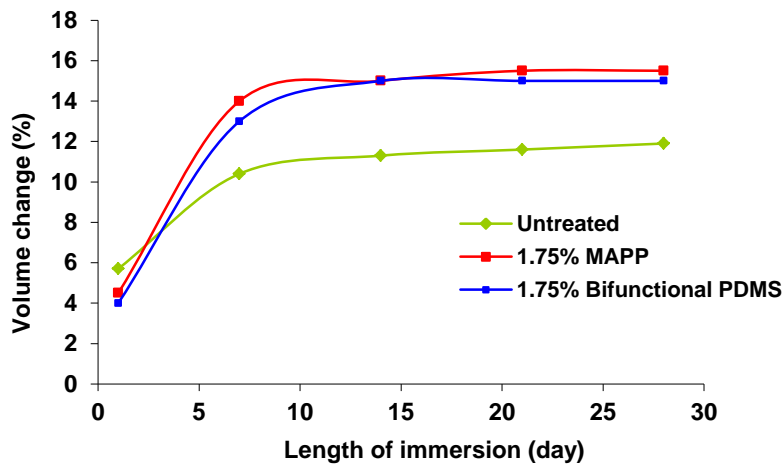


Figure 7.9: The effect of coupling agent on the volume change of 70/30 WF/PP composites

As discussed in the previous chapter, the mechanical properties of WF/PP 70/30 treated with the bifunctional PDMS have increased compared to the untreated composite. Despite the mechanical properties enhancement achieved, the treated 70/30 WF/PP composites have higher water absorption compared to the untreated composites. The PP matrix does not absorb any moisture or water (Bledzki *et al.*, 2005), indicating that water is only absorbed by the wood component in the composites. The treatment has increased the hydrophilic characteristics of the composites produced. Either MAPP or PDMS treated 70/30 WF/PP composites show the same water absorption result upon compounding (Figures 7.8 and 7.9).

It is reported that the hydrophobicity of the composites increased when MAPP was used in WPC systems. This characteristic is due to the esterification of the cellulose hydroxyl group by the anhydride functional group in MAPP (Acha *et al.*, 2007, Beldzki *et al.*, 1996) resulting in less OH group on the cellulose structure to absorb water. This reaction caused the surface energy of the wood to increase to a level much closer to the surface energy of the matrix. Thus, a better wettability and a higher interfacial adhesion are obtained. The PP chain permits segmental crystallization and cohesive coupling between the modified wood and the PP matrix (Beldzki *et al.*, 1996; Gassan & Bledzki, 2000).

However, as far as our concern, the improvements in water absorption of MAPP treated composites reported were observed with the composite system containing less than 70% wood and the water absorption measurements were done using different methods. Jahangir *et al.* (2007) observed the improvement in the WF/HDPE composites system containing 60% wood for 120 days of soaking and Bledzki and Farouk (2003) observed it with WF/PP composites containing 50% of wood and the water absorption were done for only 48 hours. Ashori and Sheshmani (2010) found the improvement in water absorption when they used MAPP in their

30% hybrid recycled cellulose and 70% recycled PP composites after 2200 hours of immersion. Jiang and Kamdem (2004) reported the improvement with WF/PVC composites system containing only 40% of wood using ASTM D1037, while Felix and Gatenholm (1991) only reported the hydrophobicity improvement from the contact angle measurement of the composites prepared by immersion of cellulose fibre in a solution of MAH-PP copolymer in hot toluene (100 °C) for five minutes, which were than Soxhlet-extracted with toluene for 48 h to remove all components not covalently bonded to the fibres. The concentration of the copolymer in solution was 5 wt% on the fibres. The reported change in the water uptake ranges between +2% to -60% (Danyadi *et al.*, 2010). Thus, we can really not compare the improvement quantitatively because of different components, compositions, processing and measurement conditions in the various studies.

The same negative observation on the use of MAPP coupling agent on the water uptake of WF/PP system was also reported recently by Danyadi *et al.*, (2010). They observed contradictory results compared to other studies in the composites system that contained 20% of wood flour in PP with 210 µm wood particle size and processed in the Brabender internal mixer. They found that the water absorption of the composites does not improve even though mechanical properties were enhanced with the use of MAPP compared to the untreated composites. They claimed the negative effect was due to the use of MAPP directly during blending without pre-treatment steps of MAPP to the wood. They expected that the decrement was either because the formed ester bonds hydrolysed or because of their small number. They also stated that the contradictions and large differences could be explained by different components, compositions and measurement conditions in the various studies.

In our study, both treated and untreated wood were oven dried prior to compounding until less than one per cent moisture content obtained. The higher water absorption in MAPP treated composites might most probably be the result from the very low retention time in the barrel during compounding and the high amount of wood in the composites. The retention time for the compounding process was only 30 seconds. It is impossible to have a longer retention time in the small compounder without any pressure controller and even any viscoelastic feature display. Furthermore, when we used larger amount of wood flour (up to 70%) in our composites, it became harder to control the compounding flow rate. So the low retention time is the expected reason to cause only part of MAPP to react with wood and PP during processing, thus, producing only a small number of ester bonds, as also stated by Danyadi *et al.* (2010). The remaining unreacted MAPP and the small number of ester bonds in the composite absorb more water compared to the untreated composite. Other than that, 30% PP in the composites with only 1.75% of MAPP to the weight of wood is far too low to adhere to the whole system. So gathering all the factors might contribute to the lower water uptake performance in MAPP treatment.

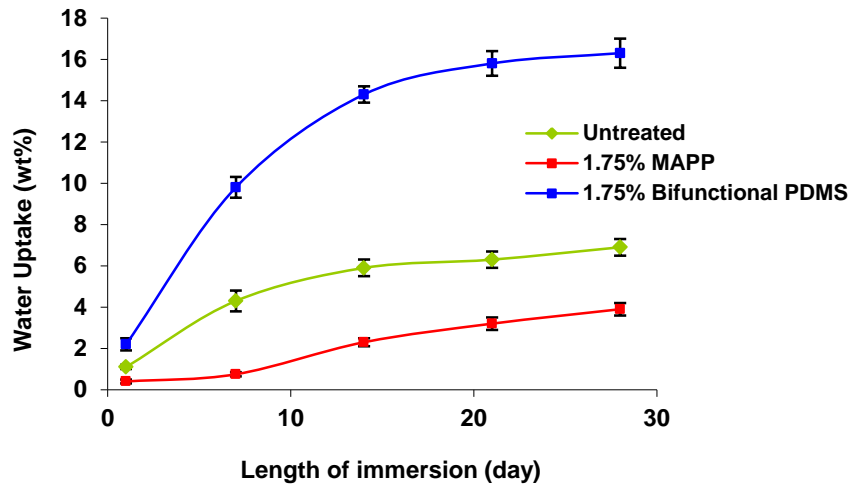


Figure 7.10: The effect of coupling agent on the water absorption of 30/70 WF/PP composites

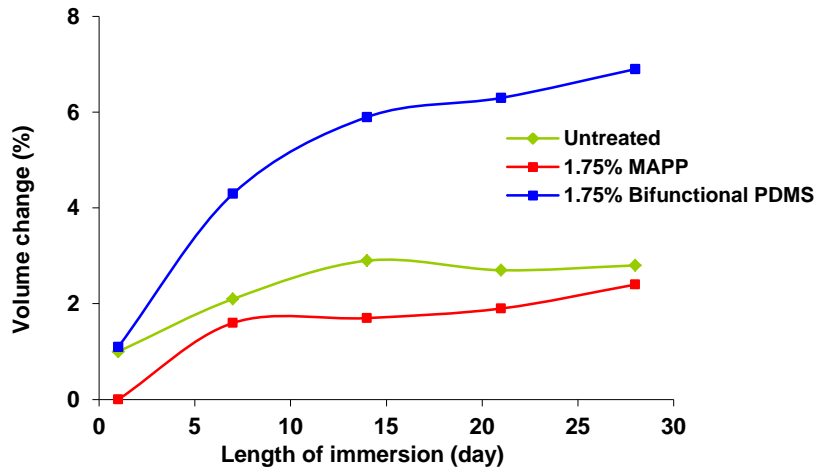


Figure 7.11: The effect of coupling agent on the volume change of 30/70 WF/PP composites

However, we can see the water absorption of MAPP treated composites containing 70% plastic has improved compared to the untreated composites (Figures 7.10 and 7.11). So these results proved that MAPP treatment actually improves the hydrophobicity characteristic of the composites. However, the effectiveness of the MAPP reaction could only be seen when more plastic was used. This is because wetting was improved when there was more plastic in the composite. The wood particles would totally be encapsulated by the plastic matrix with a better interface existing from the MAPP coupling reaction and fewer gaps existing in the interfacial region (Ashori & Nourbakhsh, 2010). This phenomenon can be described by the following *pinwheel* models proposed by Lu *et al.* (2005) showing the interface structure of composites containing different composition of wood-plastic components.

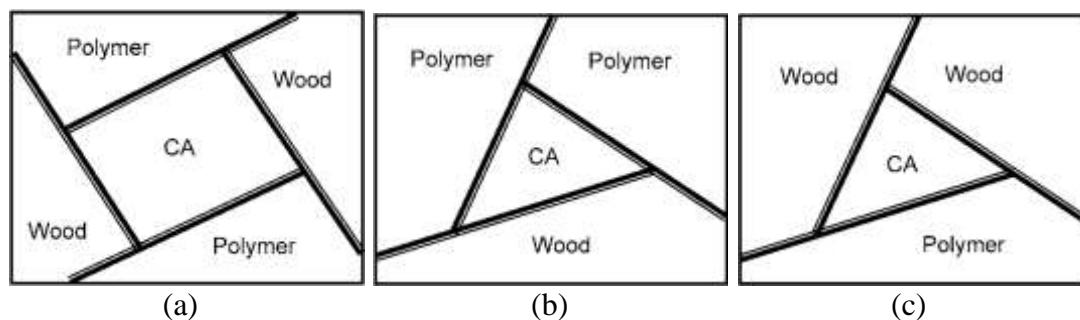


Figure 7.12: Pinwheel models of composites modified with a coupling agent's interfaces; (a) wood-polymer ratio is 50/50 (b) more polymer was used (c) more wood was used (Lu *et al.*, 2005).

From the models, the interface could be explained as; (a) is a symmetrical structure where the coupling agent is distributed at the interface to form the polymer–wood, polymer – coupling agent – polymer, polymer – coupling agent – wood and wood – coupling agent – wood interphase. Asymmetric structures (b) and (c) are suitable for treated composites when the amount of the wood is unequal to that of the polymer matrix. In structure (b), the wood is encapsulated by the polymer matrix, while in (c) too much wood caused discontinuous phase of the polymer matrix. Structure (b) has four interphases: polymer – polymer, polymer – wood, wood – coupling agent – polymer, and polymer – coupling agent – polymer. Similarly, wood – wood, wood – polymer, wood – coupling agent – polymer and wood – coupling agent – wood interphases exist in structure (c).

The models with more plastic used in the composite, clearly show that wetting from polymer plastic is very well distributed to the whole system. This is a very important factor in ensuring an improvement of water absorption in a composites system. The same can be seen from the water absorption result when 70% plastic was used with the MAPP treated composite. Lu *et al.* (2005) reported that chemical bridge has even occurred when composites containing more wood were treated with MAPP (model c). However the 70% wood treated with MAPP composite in our study does not improve the water absorption. The processing condition and method using the Theysohn compounder EKS-TSK 20 with a very short retention time is not so suitable in compounding the composite using 70% wood as discussed earlier.

Discussing the higher water absorption in very high molecular weight bifunctional triethoxy-vinyl PDMS treated composite comparing to the untreated composite give rise to a few reasons. However before we will go through into the details we should put into our mind that first of all the result shown by the Figure 4.3 demonstrate that the PDMS impregnated woods absorbs less moisture compared to the untreated wood under the same conditions. That proved the theory that the PDMS treatment has been resulting in less hydrophilic wood flour. However, the resulting PDMS treated composites have absorbed more water showing that the cause of the problem rises during composites processing and production.

The first reason is the lack of wetting from plastic component in the 70/30 WF/PP composition as discussed in the MAPP treated composite earlier. Too much wood causes that only part of it to be encapsulated by plastic matrix which is not enough to improve hydrophobicity characteristic. The second reason is the processing condition when using the small Theysohn co-rotating twin-screw extrusion compounder EKS-TSK 20. As discussed earlier, the very low retention time might cause the unfinished coupling reaction. On the other hand the very small compounder with only 2 cm in diameter of the screw, when filled up with 70% of unmelted wood particles at 280 to 350 rpm of speed, will generate a very high shear rate in the barrel. This shear stress with the influence of the coupling agent and peroxide initiator has probably broken the wood structure and produced some new side products causing the composite having more hydrophilic characteristics than before.

7.4.1 Sugar analysis and water absorption

The depolymerisation process of polysaccharides in wood to sugar monomer could also be the cause of higher water absorption problem. There are several factors influencing the depolymerisation process of wood to monomer, which are temperature, pH, catalyst, and time. The PDMS used has a pH value of 4.3 and we are convinced as well that the treatment lowered the processing temperature of the treated composites about 20% (refer to Table 3.4). Wood is very sensitive to temperature. For technical reasons described before, it was not possible to produce the same composition of treated composites at the same processing temperature as the untreated composites or the yield would be black burnt ash. From this condition, we can say that the treated wood can easier degrade. Following this statement, we can theoretically predict that some of our wood has undergone the degradation or depolymerisation process producing sugar monomers, which will give rise to OH-groups in the wood component of the composites. However, from the increments in the mechanical properties, the results of microscopy images, and the DMA analysis of the composites discussed earlier we can say that this degradation, nevertheless, does not prevent the coupling agent reaction to become an interphase in the composites. The reaction between the PP and vinyl groups still occurred and the covalent bonding between PDMS and wood are at the same time existent, while the monomer might react to each other through hydrogen bonding.

The following Figures 7.13 and 7.14 show the chromatogram of sugar analysis of the untreated and PDMS treated composites. The analysis was done using four points' standard solutions with the calibration plot of every free sugar as attached in the appendixes section. From the comparison of both chromatograms it can be seen that the amount of free sugars in the treated composite is higher. From the Tables 7.2 and 7.3, we can also see that the untreated composite contains the overall of 108 mg/L free sugar while the treated composite contains 160 mg/L free sugar, which is 48% more. The free sugars found in the untreated composite were detected to be glucose, arabinose, galactose and xylose while in the treated

composite beside the same sugars, one more sugar nominal cellobiose with only 0.5 mg/L was also detected.

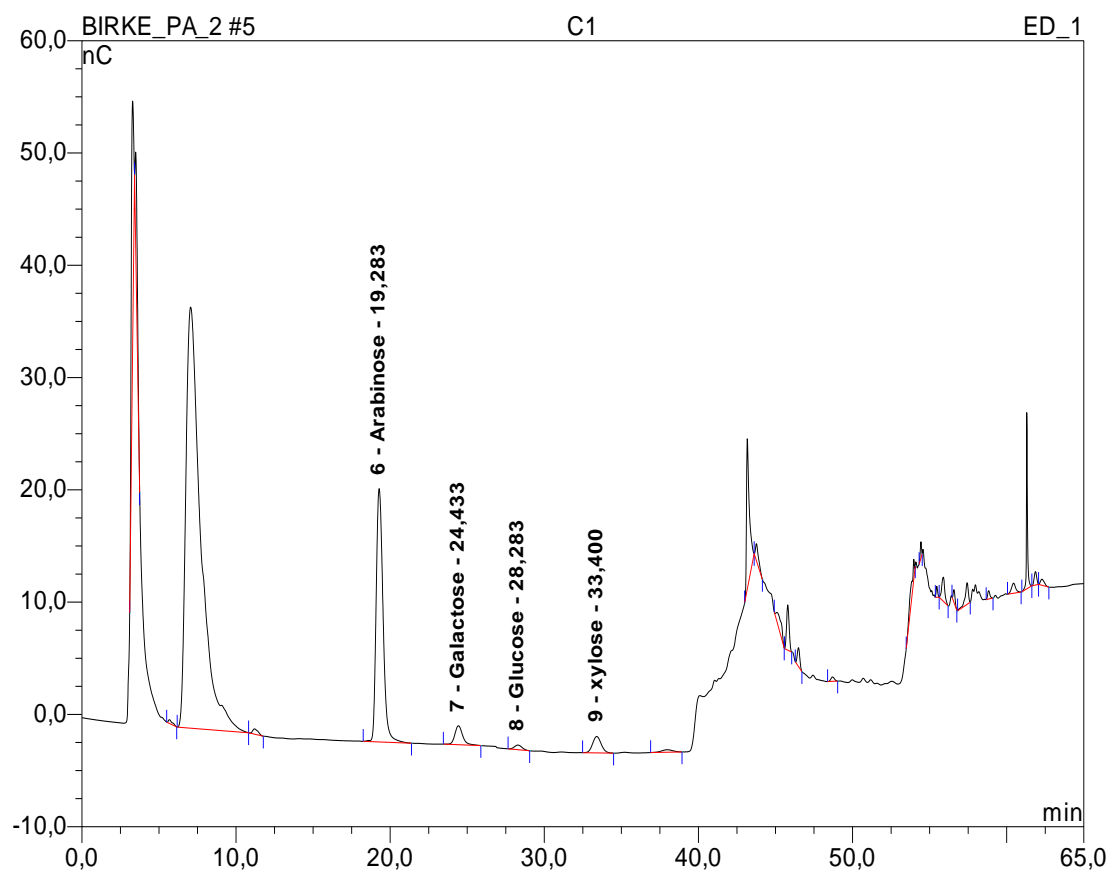


Figure 7.13: Chromatogram of sugar analysis for untreated 70/30 WF/PP composite

Table 7.2: Sugar content for untreated 70/30 WF/PP composite

Peak No.	Retention Time (min)	Peak Name	Height (nC)	Area (nC*min)	Relative Area (%)	Amount (mg/L)
6	19.3	Arabinose	22.6	11.7	16.4	96.5
7	24.4	Galactose	1.7	1.0	1.4	5.0
8	28.3	Glucose	0.4	0.2	0.3	0.9
9	33.4	Xylose	1.5	1.0	1.3	5.1
Total:			26.1	13.8	19.5	107.5

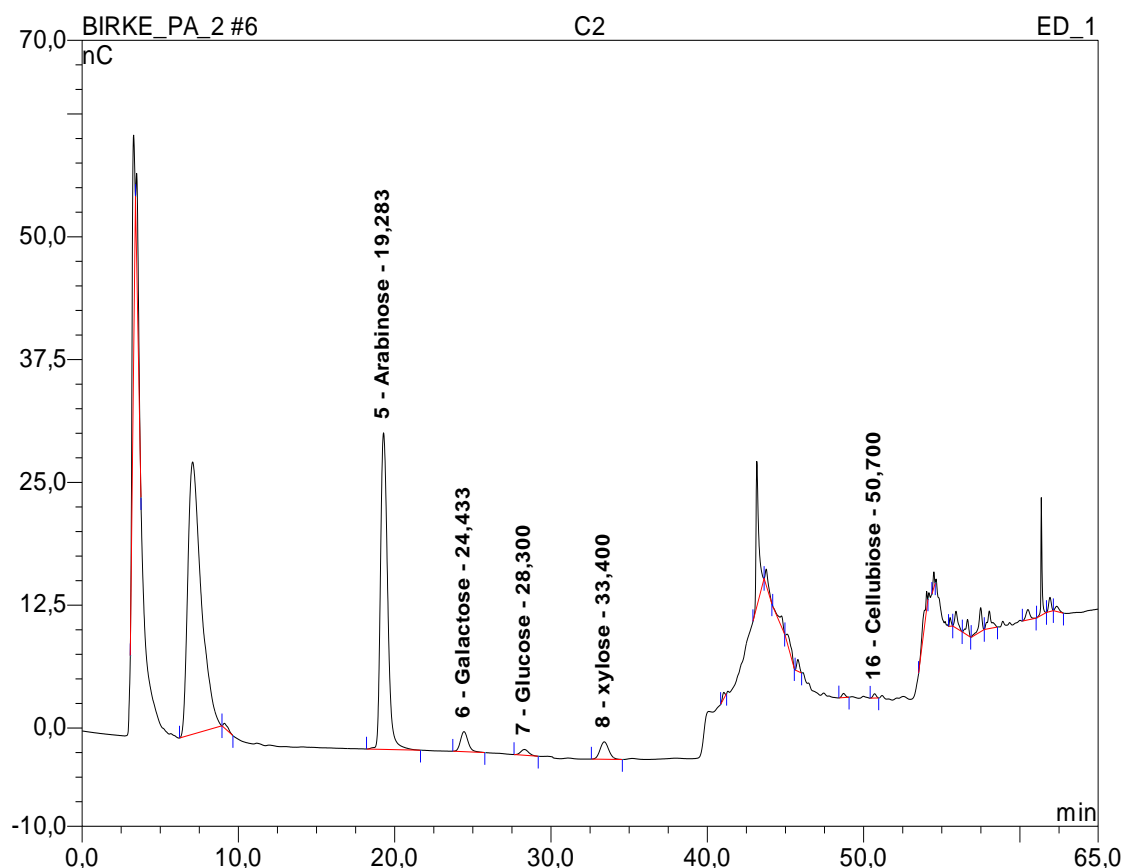


Figure 7.14: Chromatogram of sugar analysis for 70/30 WF/PP composite treated with 1.75% very high molecular weight bifunctional triethoxy-vinyl PDMS

Table 7.3: Sugar content for 70/30 WF/PP composite treated with 1.75% very high molecular weight bifunctional triethoxy-vinyl PDMS

Peak No.	Retention Time (min)	Peak Name	Height (nC)	Area (nC*min)	Relative Area (%)	Amount (mg/L)
5	19.3	Arabinose	32.2	17.0	27.2	146.1
6	24.4	Galactose	2.0	1.2	1.8	5.8
7	28.3	Glucose	0.6	0.3	0.6	1.3
8	33.4	Xylose	1.8	1.2	1.8	6.2
16	50.7	Cellubiose	0.4	0.1	0.2	0.5
Total:			37.1	19.8	31.6	159.9

Basically two of the three lignocellulosic materials are made of repeating units of the monosaccharide units of various types. The basic unit of cellulose is ‘cellobiose’. Hydroxyl group of cellulose makes fibrils by forming hydrogen bond with hydroxyl groups neighbouring other cellulose molecular chains and partially

crystallizes (Park *et al.* 2008). Hemicellulose composes of many kinds of carbohydrate complex that is similar to the chemical composition of cellulose, but its molecular weight is smaller, that is around 200 sugar units. Hemicellulose is derived from several sugars in addition to glucose, especially xylose but also mannose, galactose, rhamnose, and arabinose. Furthermore, hemicellulose is branched, whereas cellulose is unbranched (Ishii and Shimizu, 2001). All these monosaccharides are together joint to each other by glycosidic bonds to form polysaccharides.

The absorption of water by different wood-based composites is largely dependent on the availability of the free –OH groups on the surface of the reinforcing fibre in the composites (Ashori & Nourbakhsh, 2010). In a polysaccharide form, all the sugar monomer contains three free hydroxyl groups (Figure 7.15 (a)) that could react or form hydrogen bonding with water. That is why wood will normally contain an average of 8% to 10% of moisture. However, every free sugar monomer will contain five free hydroxyl groups if the polysaccharide has been hydrolysed (Figure 7.15 (b)). The broken glycosidic linkage will be substituted with the hydroxyl group and become more hydrophilic. That is why the composites treated with 1.75% very high molecular weight bifunctional triethoxy-vinyl PDMS have higher water absorption compared to the untreated composite. Obviously, the hydrolysed sugars originate from the hemicellulose, which is amorphous, and easier to be depolymerized while 0.5 mg/L of cellobiose found might come from some slight decomposition of cellulose as well.

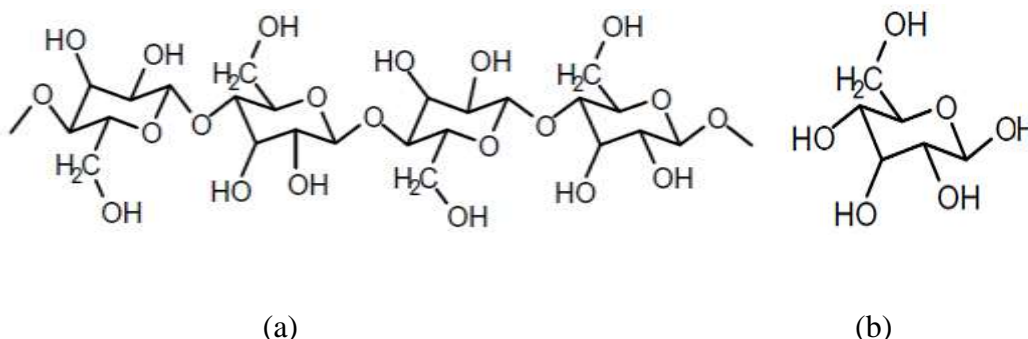


Figure 7.15: (a) Three free hydroxyl group exist in every monomer in a polysaccharide structure and (b) five free hydroxyl group exist in a monomer structure

The water absorption results for treated composite containing 30/70 WF/PP (Figures 7.10 and 7.11) are obviously supporting our analysis that bifunctional PDMS treated composite containing 0.1% DCP compounded with the small Theysohn compounder EKS-TSK 20 has caused partial hydrolysis of the lignocellulose materials. These results in higher water absorption of the bifunctional treated composite compared to the untreated composite even when 70% plastic was used.

8 The effect of treatment conditions and PP composition on WPC performance

There are several ways or methods to apply the coupling agents during the WPC production process. Depending on the form of coupling agent been used, the available equipment and the chosen method, the outcomes or the effectiveness of the treatments is varied. Every preparation will produce its own WPC characteristics. Here we can see the different outcomes of the same coupling agent of distinct types and applied using dissimilar methods of treatment. The coupling agent is very high molecular weight bifunctional triethoxy-vinyl PDMS and the conditions are:

- TEGOMER V-Si 4042 batch VB 3248, 100% purity in liquid form.
 - Treatment was applied using impregnation procedure prior to compounding as described in Chapter 3 section 3.2.1.
- TEGO XP 6000 batch 294; 50% master batch VB3248 compounded in Polypropylene.
 - Treatment was applied using in situ processing, direct compounding as described in Chapter 3 section 3.2.3.
- TEGOPREN 6875-45 batch 3248; 50% emulsion of VB 3248
 - Treatment was applied by spraying the coupling agent onto the wood flour surfaces in a dry mixer prior to compounding as described in Chapter 3 section 3.2.3.

All processing conditions applied during compounding following treatments (impregnation and spraying method) were the same as the in situ processing condition of the TEGO XP 6000 batch 294. The following figures show the results of the WPC produced.

8.1 Mechanical properties

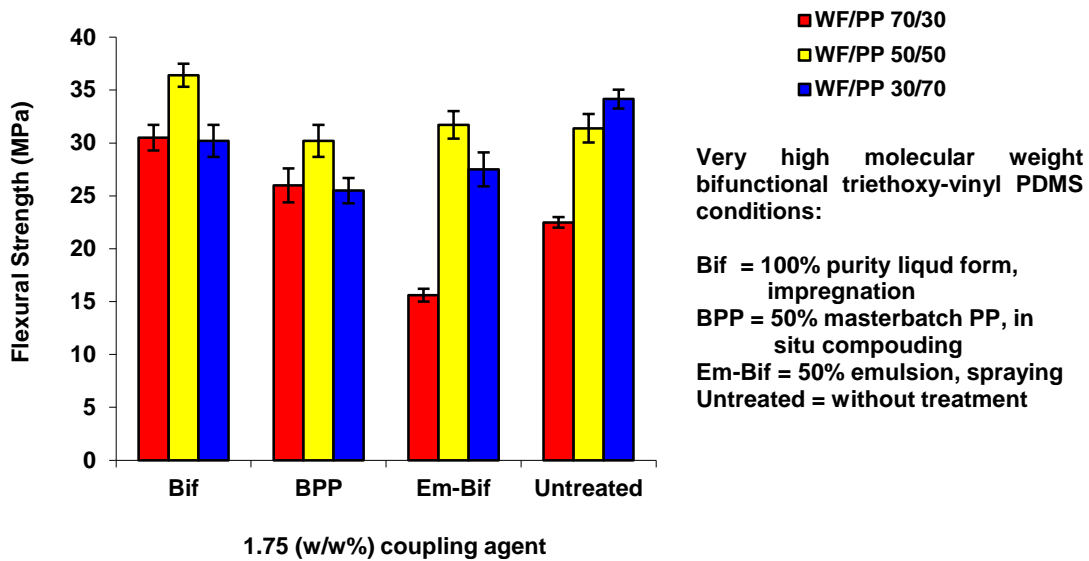


Figure 8.1: The effect PDMS conditions and method of treatment application on WF/PP composites flexural strength with different WF/PP composition.

Among all treated composites, the highest flexural strength was obtained from impregnation treatment (Bif) (Figure 8.1) for all matrix compositions. It was followed by the in situ compounding method (BPP) if more wood was used in the composites or with the spraying method (em-Bif) if more plastic was used in the composites. The 50/50 WF/PP composition shows more or less the same strength for both BPP and Em-Bif, but the impregnation of Bif still gives the highest strength.

However, compared to the untreated composites, spraying the em-Bif has a negative effect to the composites when more plastic (WF/PP 30/70) or more wood (WF/PP 70/30) was used and no improvement occurred with the 50/50 composition. BPP only improved the strength when more wood was used in the composites, no improvement on the 50/50 composition was observed and decreased when more plastic was used in the composites. Impregnation of Bif gives the best results with the enhancement of 70/30 and 50/50 WF/PP composites' strength compared to the untreated composites, but still decreases when more plastic was used.

These results show that impregnation is the best procedure to apply PDMS, contributing to a better reaction of PDMS coupling agent during compounding. This is because the PDMS has enough retention time to disperse evenly into the wood (Hill, 2006). Furthermore, the vacuum condition leads to the dispersion of PDMS coupling agent not only on the surface but also deep into the cell wall raising the possibility of covalent bond formation.

Moreover, for 70/30 WF/PP composition, the BPP reacted better than the Em-Bif spraying technique because PDMS have already compounded with one of the components that is PP, giving them more opportunities in bonding. Though, the low retention time in the compounder still limits the coupling agent bonding reaction

with wood. It is expected that only some of the triethoxy functional group have time enough to undergo covalent bonding with wood while the other just performs hydrogen bonding.

Spraying the em-Bif decreases the performance. As we could see previously (in Chapter 5) the addition of PDMS will decrease the mechanical properties if no DCP was used to initiate the reaction. In this case, it seems that the coupling reaction does not occur. 100 ml of emulsion PDMS were sprayed onto 3000 g of wood flour surfaces. Thus, 15 minutes of spraying time might not be sufficient to disperse the emulsion PDMS to the whole wood flour surfaces and carry out bonding. Comparing to the impregnation, this method gives the possibilities of PDMS to react only on the surfaces of the wood particles. Furthermore, the sprayed wood flour was directly compounded without prior heating causing fewer possibilities of covalent bonding between triethoxy groups to the wood when the retention time in the compounder was too low.

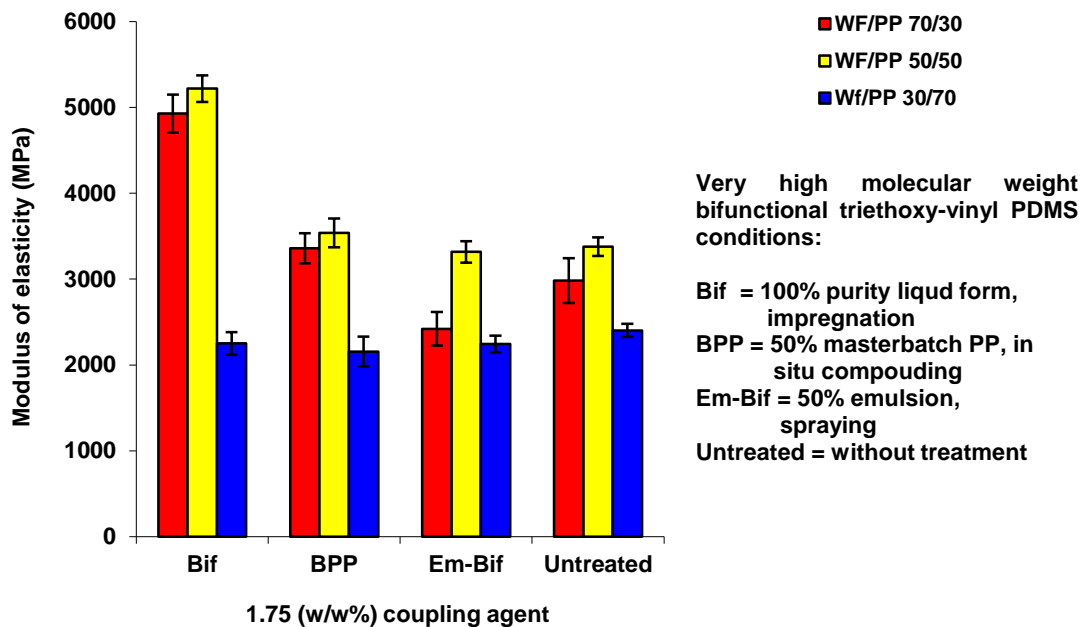


Figure 8.2: The effect PDMS conditions and method of treatment application on WF/PP composites modulus of elasticity with different matrix composition

Composites prepared with the impregnation procedure showed the highest modulus of elasticity resulting from better adhesion of coupling agent. As shown in Figure 8.2 all formulations have the same trend of stiffness with 50/50 compositions having the highest stiffness in all conditions. This is because the influence of plastic component in performing wetting to the whole wood surfaces when the wood-plastic composition is to the same ratio. These results also proved that the modulus of elasticity is not influenced by the addition of coupling agent, unless good adhesions occurred.

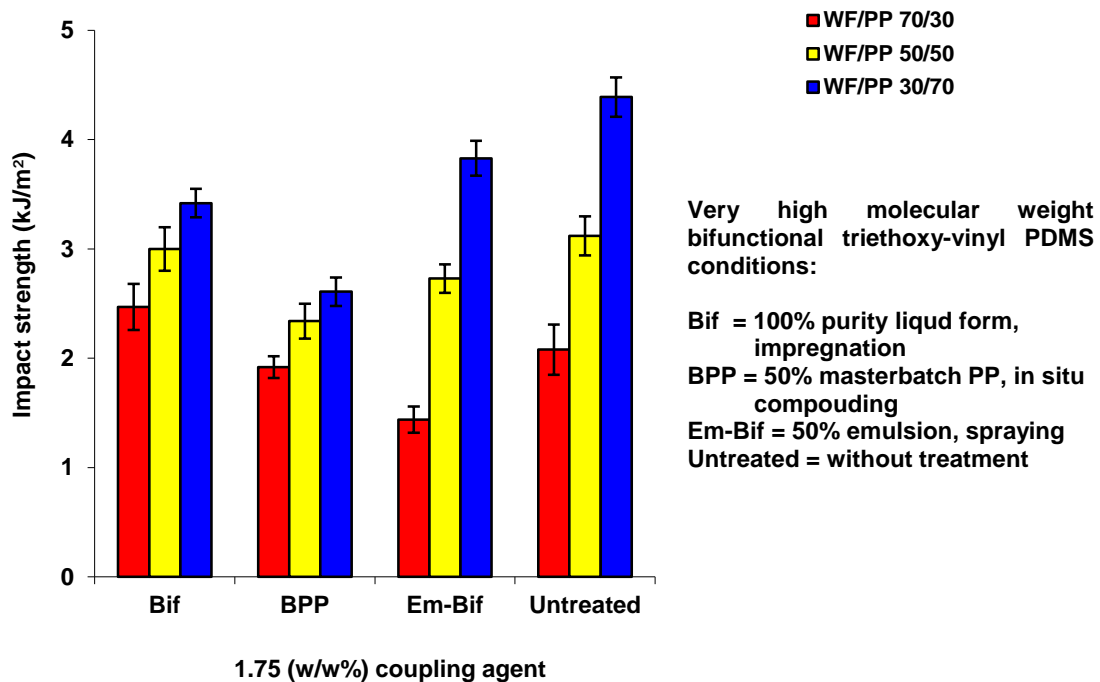


Figure 8.3: The effect PDMS conditions and method of treatment application on WF/PP composites impact strength with different matrix composition

Figure 8.3 shows that impact strengths of the composites are more affected by the matrix composition. The higher PP content increases the ability of composites to withstand the impact and prevent breakage and it can be seen that the highest impact strength is obtained from the untreated composite with 70% PP. As discussed earlier, DCP reaction in the treated composites have caused chain scission during processing. This is probably the reason for lower impact strength obtained with the treated composites even when 70% PP was used. In the case of Em-Bif treated composites, there might be too little or almost no coupling reaction or adhesion occurred resulting in the very similar trend to the untreated composites but with lower values. Em-Bif maybe also acts as impurity in the systems and destroys the original interaction between wood and plastic.

On the other hand, with Bif and BPP treatments, where good adhesion occurred, another trend similar to each other regarding different WF/PP compositions becomes obvious. However, BPP shows lower values representing lower adhesion in the composites. Besides the matrix composition, good adhesion will prevent the propagation of crack during impact breakage resulting in higher impact strength in the composites with 70% wood when treated with Bif compared to BPP.

8.2 Water absorption

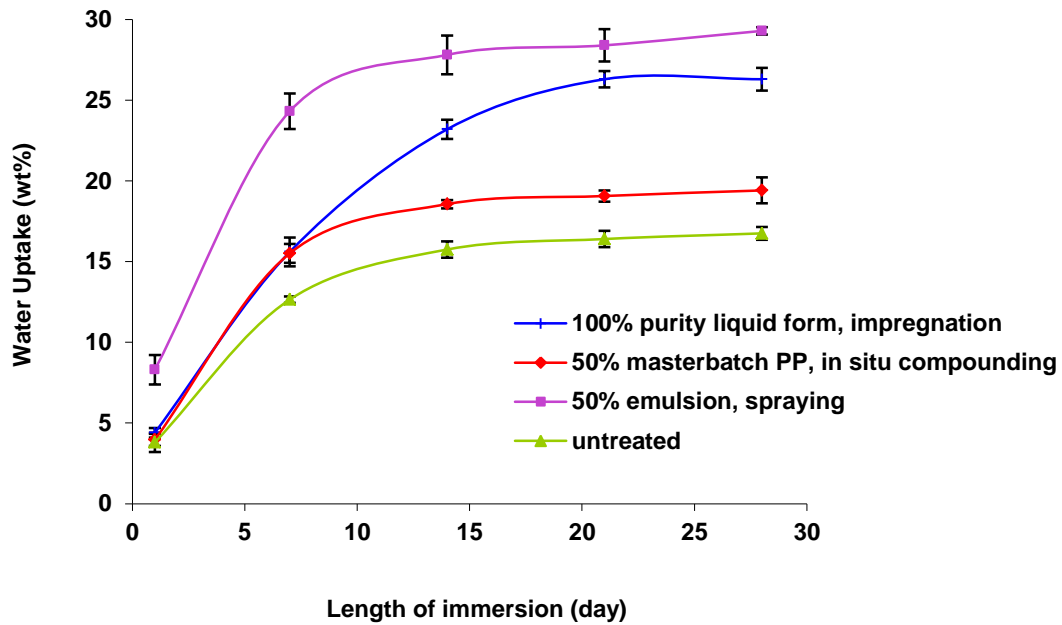


Figure 8.4: Influence of 1.75% different conditions very high molecular weight bifunctional triethoxy-vinyl PDMS on the water absorption of 70/30 WF/PP composites

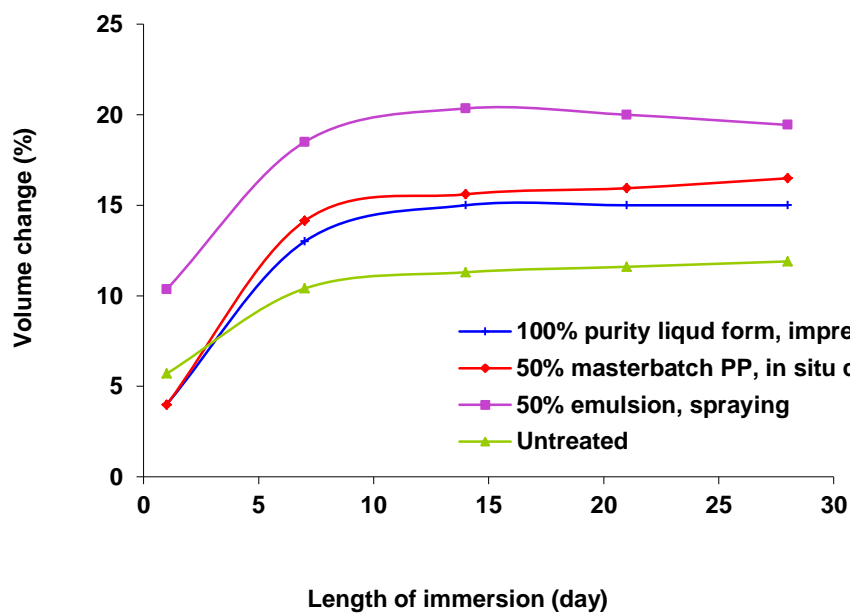


Figure 8.5: Influence of 1.75% different conditions very high molecular weight bifunctional triethoxy-vinyl PDMS on the volume change of 70/30 WF/PP composites

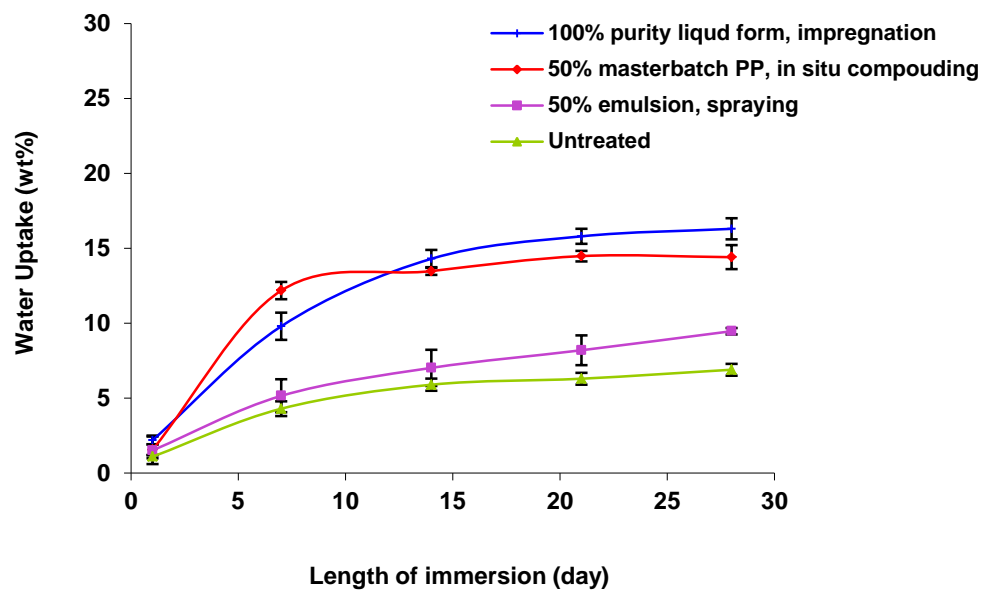


Figure 8.6: Influence of 1.75% different conditions very high molecular weight bifunctional triethoxy-vinyl PDMS on the water absorption of 30/70 WF/PP composites

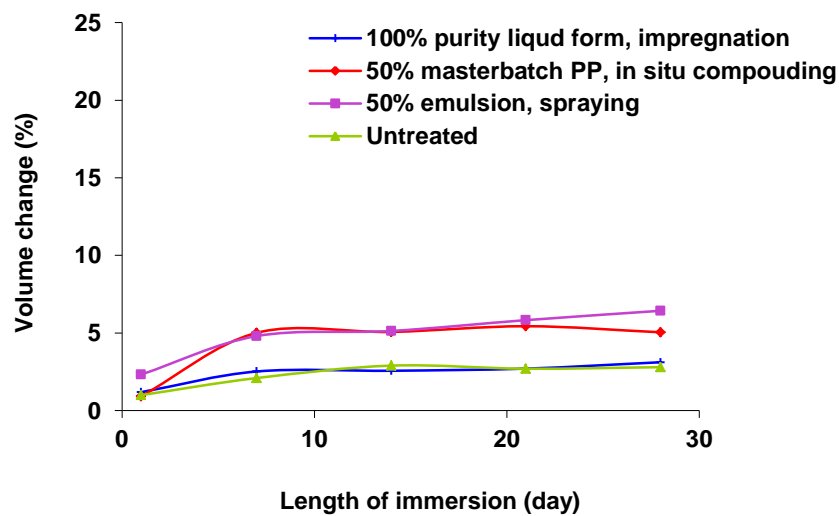


Figure 8.7: Influence of 1.75% different conditions very high molecular weight bifunctional triethoxy-vinyl PDMS on the volume change of 30/70 WF/PP composites

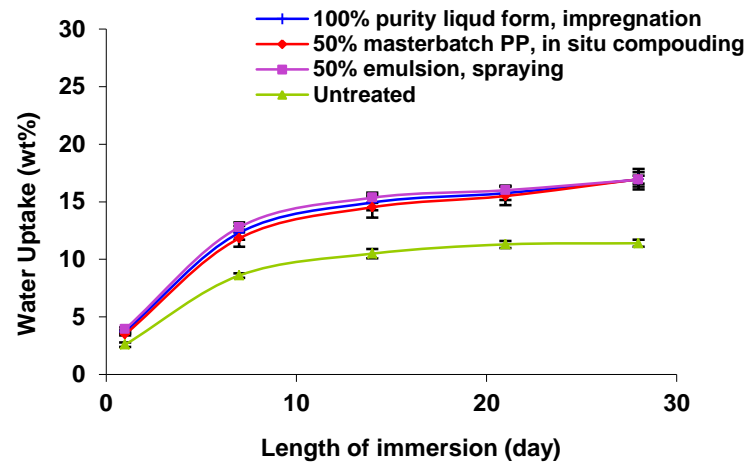


Figure 8.8: Influence of 1.75% different conditions very high molecular weight bifunctional triethoxy-vinyl PDMS on the water absorption of 50/50 WF/PP composites

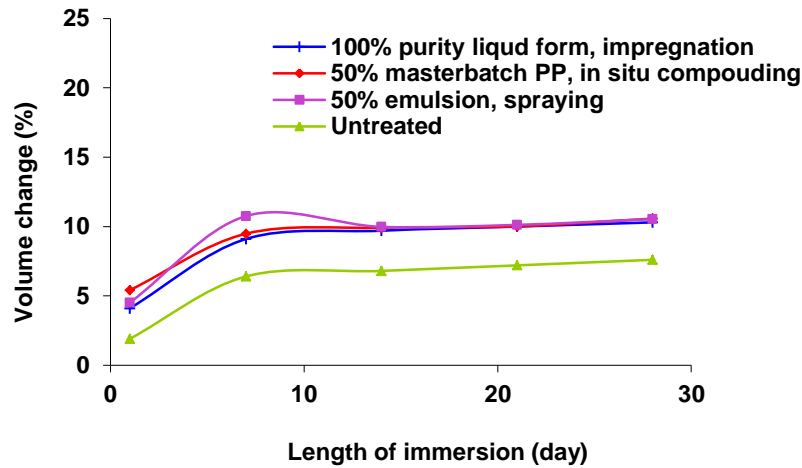


Figure 8.9: Influence of 1.75% different conditions very high molecular weight bifunctional triethoxy-vinyl PDMS on the volume change of 50/50 WF/PP composites

The water absorption values of all treatment conditions and composite compositions are higher than those of the untreated composites. Composites using impregnation method, containing more wood (WF/PP 70/30) showed the best results regarding mechanical properties, followed by in situ compounding method and spraying method (Figures 8.1 – 8.3). As discussed before, the improvement of mechanical properties using impregnation method and in situ compounding method might be due to better adhesion achieved. Higher water absorption of these two methods compared to the untreated composite (Figure 8.4) is due to hydrolysis of wood probably induced by the PDMS treatment, as shown by the results of the sugar analyses of PDMS treated and untreated composites in Chapter 7, Figures 7.13 and 7.14. Assuming the polysaccharide chain undergo hydrolysis during coupling reaction of PDMS, that might explain higher water absorption of impregnation method compared to in situ compounding method.

Figure 8.4 show that composite with spraying method of treatment absorbed the highest amount of water. This might be due to the existence of more hydroxyl functional group coming from the coupling agent and from the hydrolysed free sugar. From the mechanical performance, it could be seen that theoretically no coupling reaction has occurred in this composite leaving the unreacted hydrophilic functional groups from the coupling agent and the unreacted hydroxyl group from wood flour which will absorb more water.

When higher amount of plastic was used in the composites (WF/PP 30/70) we can see that the spraying method absorbs less water compared to impregnation and in situ compounding process (Figure 8.6). This is because the lower wood content means lower amount of PDMS in the composites, producing fewer hydroxyl functional group, thus absorbed less water.

The volume change of almost all composites with treatment conditions is higher than the untreated composites (Figures 8.5 and 8.7). Only the impregnation method with 30/70 WF/PP has the volume change comparable to the untreated composites (Figure 8.7). Comparing the treated composites, the impregnation method shows better result in volume change that is most probably because the cell wall have been swollen with PDMS during impregnation process, resulting in dimensional stability as also reported by Hill (2006).

However, having the same ratio of wood flour and PP in the composites (50/50) shows no difference between the treatments conditions regarding both water absorption and volume change (Figures 8.8 and 8.9). This is probably due to the positive effect of the higher amount of plastic and the negative effect of the hydrolysis has cancelled each other giving no significant difference.

8.3 DMA analysis

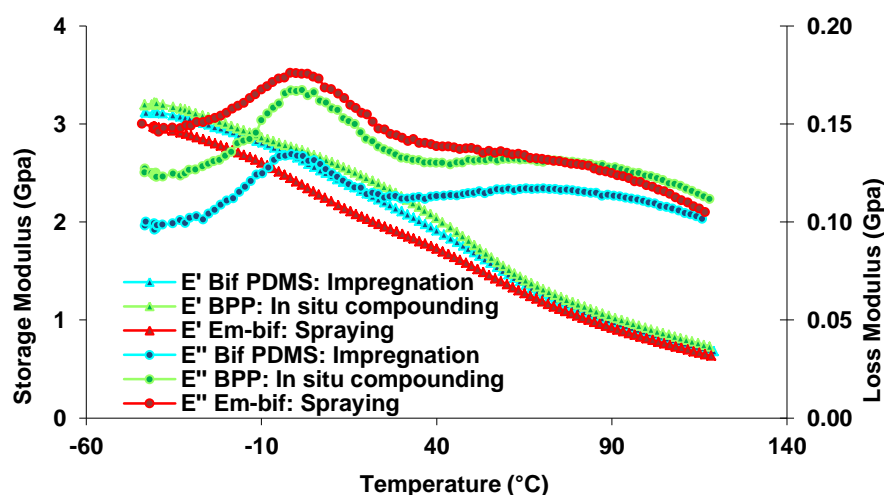


Figure 8.10: Storage modulus and loss modulus comparison of 70/30 WF/PP composites treated with different bifunctional PDMS conditions

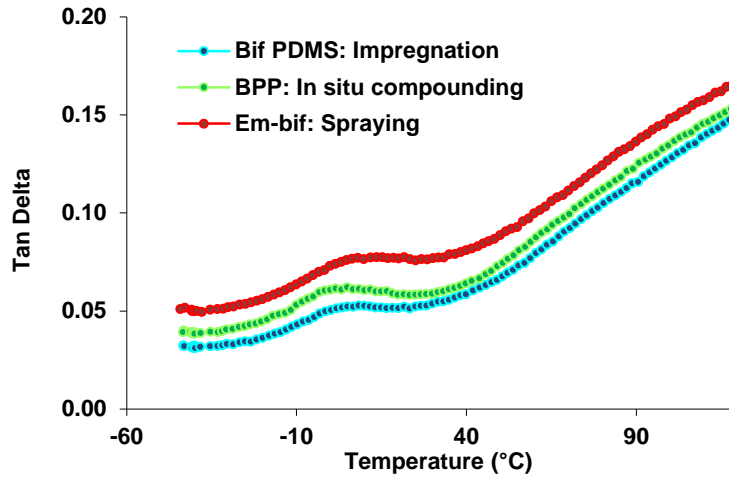


Figure 8.11: Tan delta peak comparison of 70/30 WF/PP composites treated with different PDMS conditions at 1Hz of frequency

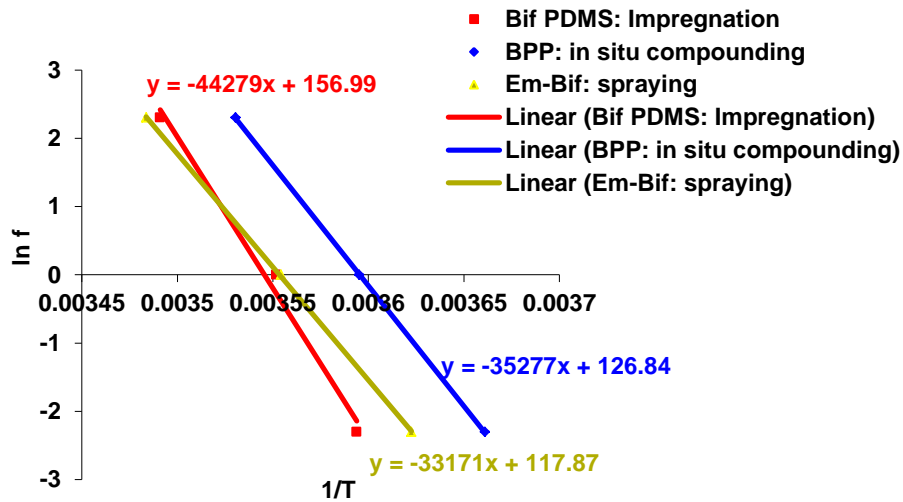


Figure 8.12: Arrhenius plot of 70/30 WF/PP treated with different PDMS conditions

The results of the DMA analyses also support the results of mechanical tests. We can see that impregnation treated composite with 70/30 WF/PP composition gives the highest activation energy for the glass transition calculated from the Arrhenius plot, as shown in Figure 8.12. Composite treated with the impregnation method achieved the highest E_a of 371 ± 3 kJ/mol following by in situ compounding composite with E_a of 294 ± 3 kJ/mol and the spraying treated composite with 274 ± 1 kJ/mol. The higher activation energy means that better adhesion existed in the composites as discussed previously in Chapter 5.

8.4 Microscopic analysis

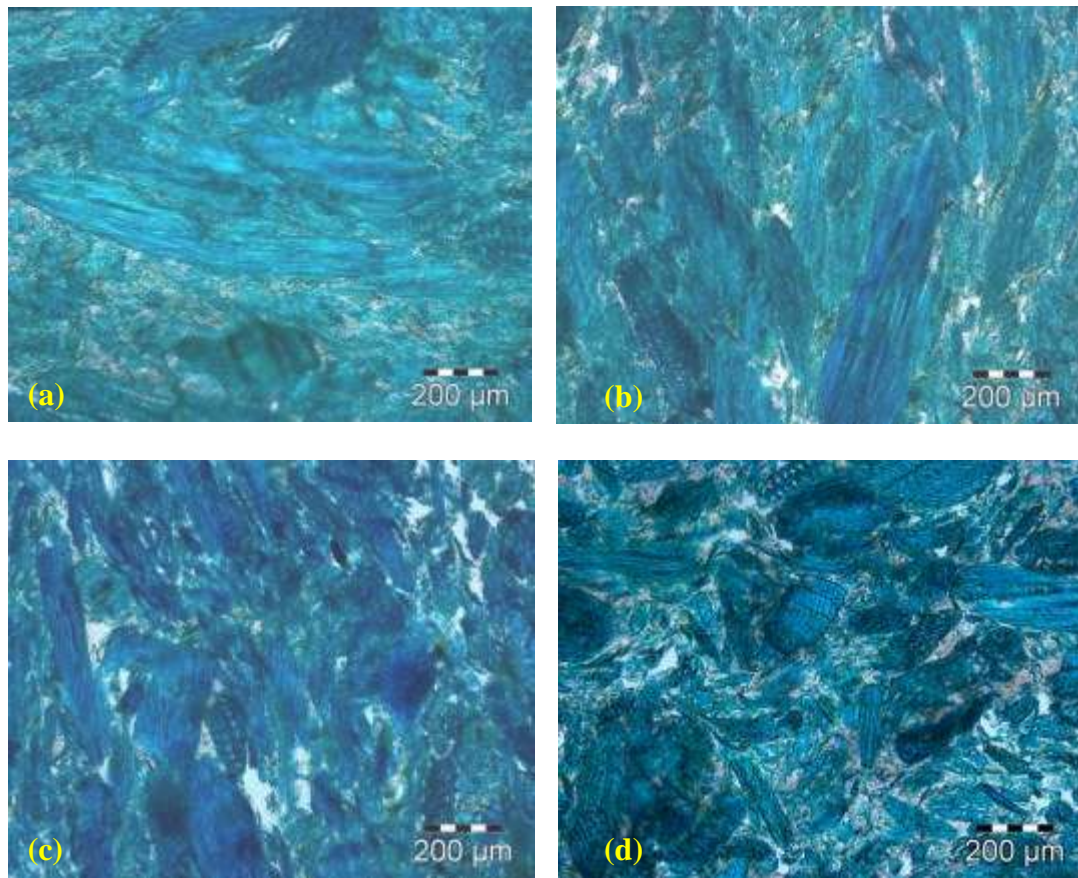


Figure 8.13: Microscopic images of 70/30 WF/PP composites treated with different treatment conditions of 1.75% very high molecular weight bifunctional triethoxy-vinyl PDMS: (a) 100% purity liquid, impregnated, (b) 50% master batch PP, in situ compounded, (c) 50% emulsion, sprayed and (d) untreated.

From the microscopic images in Figure 8.13 we can see the difference in the composites' structures containing 70% wood. The impregnation treatment with a better adhesion results in a very homogeneous structure, while some voids could be found in the in situ compounded of 50% master batch PP. In the composite treated with the spraying method, voids can be seen everywhere being worse than the untreated composites.

The following images in Figure 8.14 of composites containing 70% PP also show the same effects. Composites voids can be seen in all samples but the most could be seen in the composites treated by in situ compounding and spraying method. The untreated composite shows the best homogeneous structure.

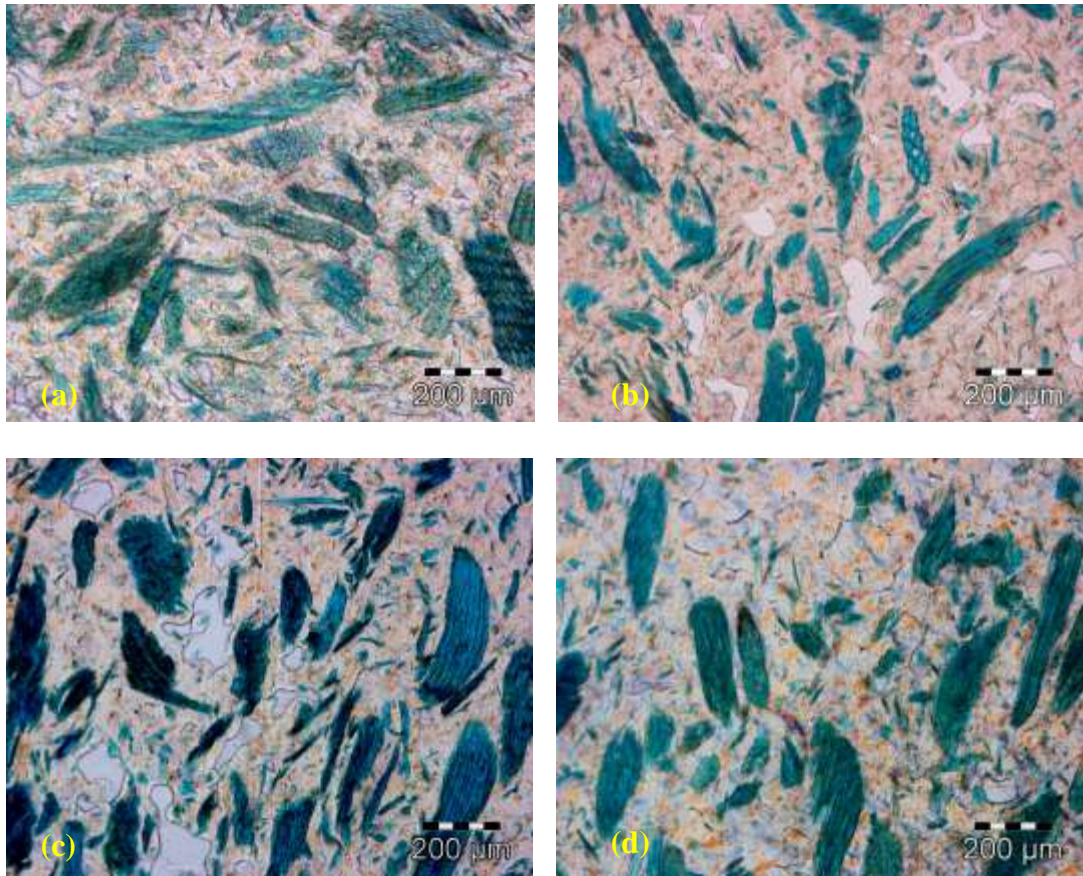


Figure 8.14: Microscopic images of 30/70 WF/PP composites treated with different treatment conditions of 1.75% very high molecular weight bifunctional triethoxy-vinyl PDMS: (a) 100% purity liquid, impregnated, (b) 50% master batch PP, in situ compounded, (c) 50% emulsion, sprayed and (d) untreated.

9 Evaluating the performance of very high molecular weight bifunctional triethoxy-vinyl PDMS and MAPP treated WF/PP composites: Particle size, re-compounding and pre-mixing

9.1 The effect of particle size on the properties of 70/30 WF/PP composites

There are two main variables that distinguish wood flour: species and particle size (Stark & Berger, 1997). Different species contain varies characteristics while the distinct particle sizes give dissimilar effects on the composites' performance. As reported by Renner *et al.* (2010) the properties of WF/PP composites depend strongly on interfacial adhesion and on the particles' characteristics of the wood. It was also reported by Myers *et al.* (1991) that particle sizes affect the properties of polypropylene filled with nominal 20-mesh and 40-mesh wood flour.

Previously, we have proven that interfacial adhesion provided by very high molecular weight bifunctional triethoxy-vinyl PDMS has enhanced the properties of 70/30 WF/PP composites composed of selected conifers wood flour with cubic structure sizes 0.3 mm – 0.5 mm. This subchapter is to discuss and investigate if larger particle size of wood could perform better when they have a thin, longer shape fibre as illustrated in Figure 9.1. The wood particle of three different particle sizes were used for comparison: wood flour with particle size of 0.3 mm – 0.5 mm (performances were presented in the previous chapters), wood particle size of 0.6 mm - 1.25 mm (mid-WP) and wood particle size of 1.25 mm - 3.15 mm length (long-WP). A better stress transfer is expected if these larger particles were used in the composites when they are well adhered with the PDMS coupling agent. 50% master batch of very high molecular weight bifunctional PDMS coupling agent in PP was used for easier processing. MAPP coupling agent was also used to confirm the results of the 50% master batch of very high molecular weight bifunctional PDMS in PP coupling agent. The following figures show the results.

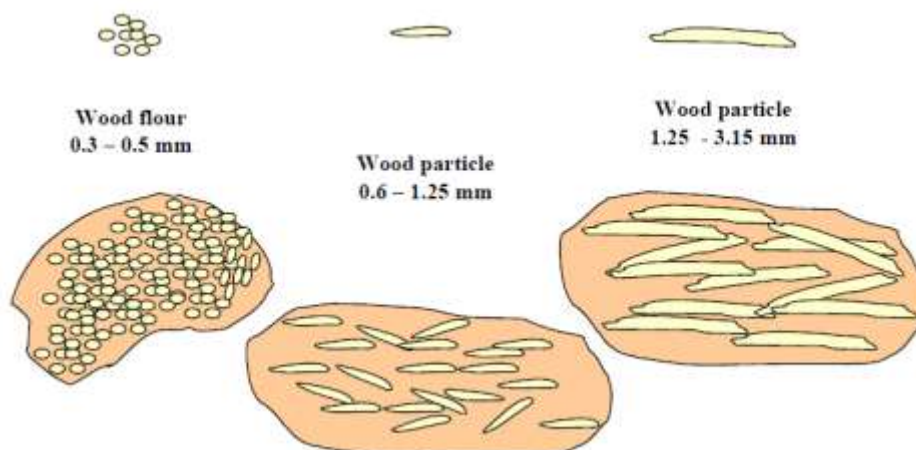


Figure 9.1: Different particle size of wood

9.1.1 Mechanical properties

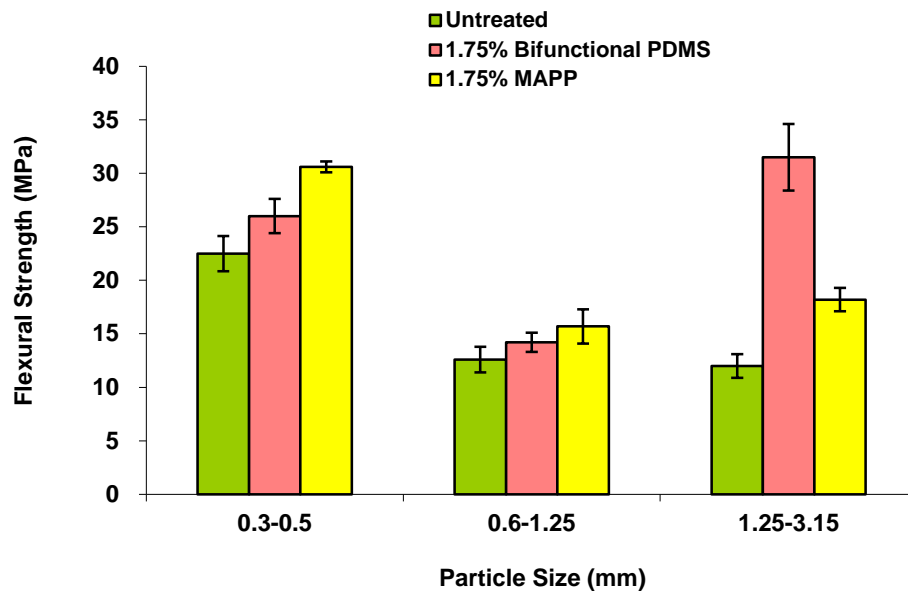


Figure 9.2: Influence of wood particle size on 70/30 WF/PP flexural strength with different coupling agent

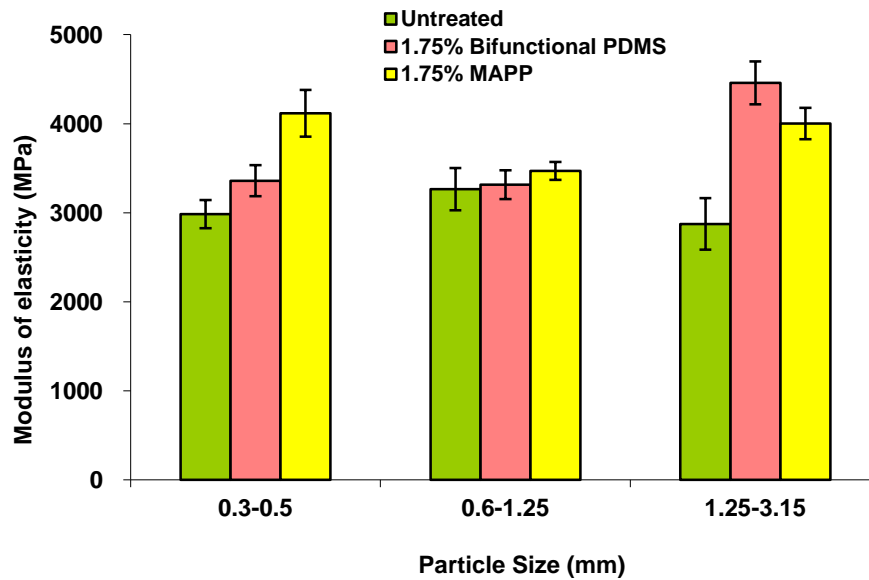


Figure 9.3: Influence of wood particle size on 70/30 WF/PP modulus of elasticity with different coupling agent

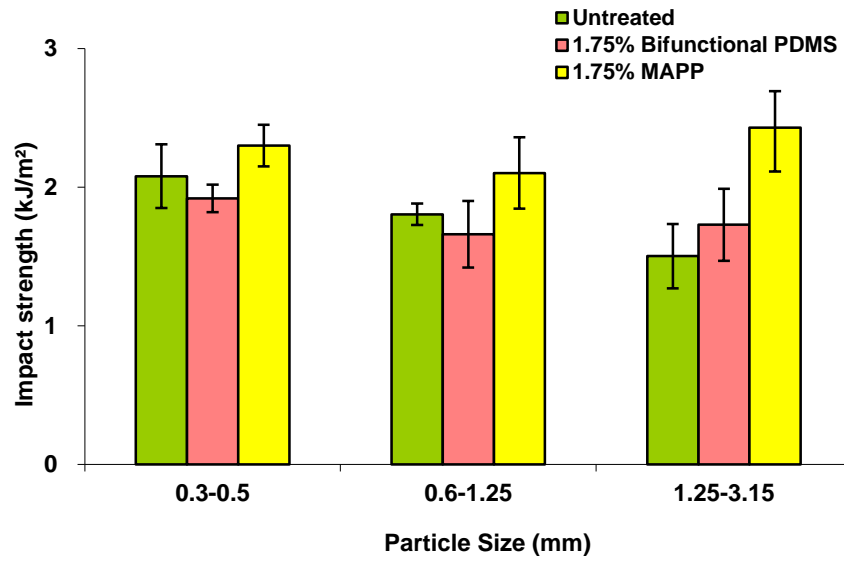


Figure 9.4: Influence of wood particle size on 70/30 WF/PP impact strength with different coupling agent

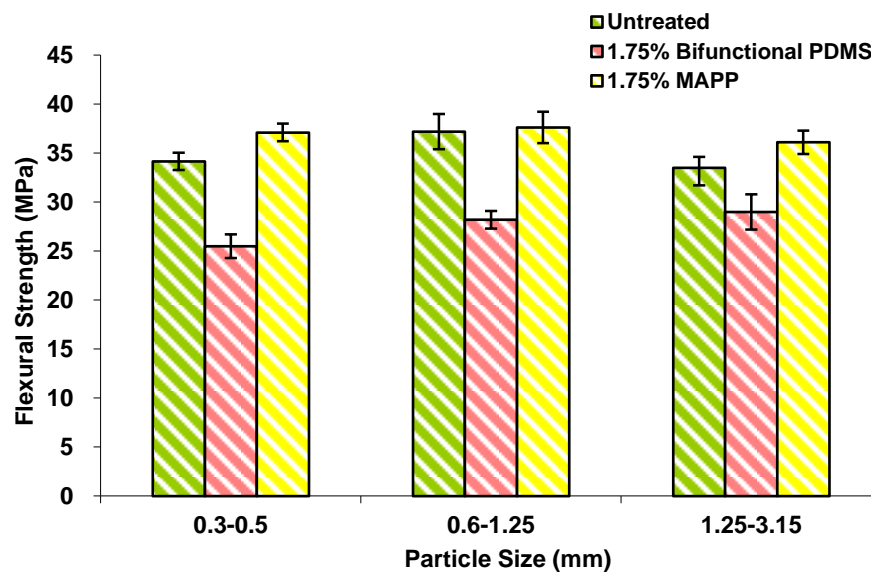


Figure 9.5: Influence of wood particle size on 30/70 WF/PP flexural strength with different coupling agent

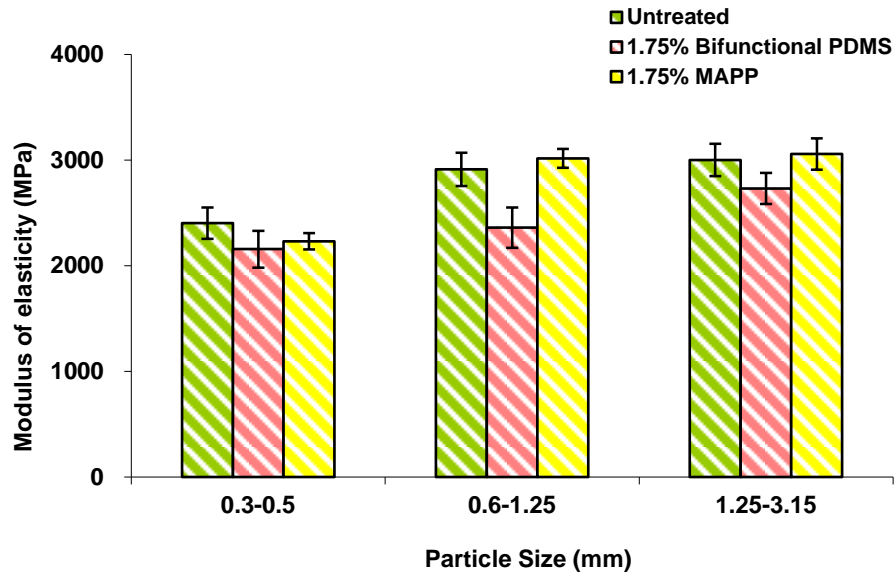


Figure 9.6: Influence of wood particle size on 30/70 WF/PP modulus of elasticity with different coupling agent

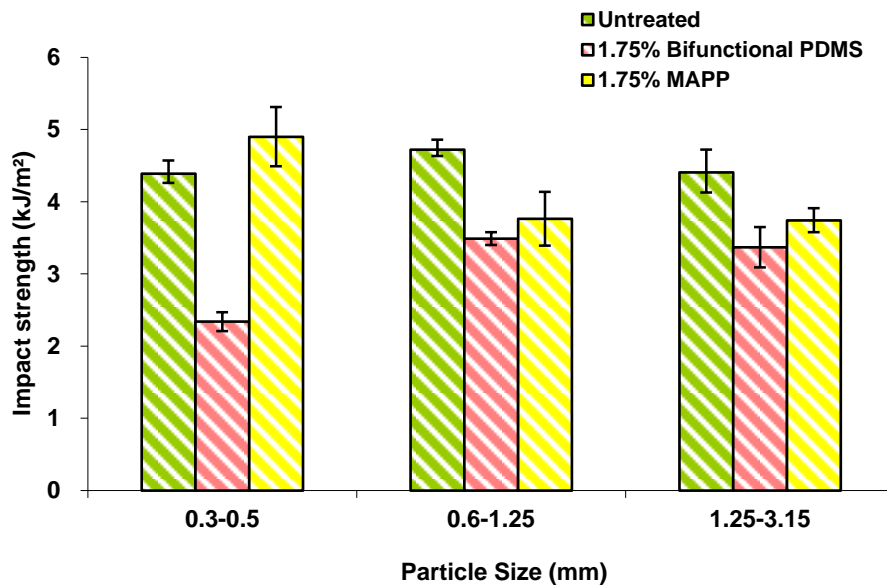


Figure 9.7: Influence of wood particle size on 30/70 WF/PP impact strength with different coupling agent

The results clearly reveal that an increasing particle size does not improve the mechanical properties of the composites. Reasons for this finding are:

- Particle breakages during compounding.

- High processing speed leading to increased shear rate in the barrel when bigger particles were used with the little compounder screw.
- The original long and thin starting particles end up smaller, and of various shapes with the increasing particle-particle, particle-screw and particle-barrel interaction. No matter how long the starting particle size was, they will end up in average range shorter than 0.6-1.25 mm, but anyway much bigger than the wood flour, thus resulting in less efficient stress transfer when load was applied to the composites during mechanical testing.

Furthermore, the larger particles are not so suitable to be processed with the small compounder. The feed port could not feed the wood particles efficiently because of their size. It was observed that sometimes they tend to remain on the top of the compounder screw in the feeding zone instead of flowing through them or they flow at a lower speed inside the barrel. They could also hardly flow through the feeder and the biggest particles (long-WP) often stuck inside the feeder being hardly controllable. These feeding and transporting problems might cause uneven composition of composites during compounding. The effect of uneven composition could be seen with higher flexural strength of composite containing 70% long-WP treated with PDMS (Figure 9.2). The strength has improved more than 100% and is even higher than the composites treated with MAPP. This result was not expected because of the poor performance exhibited by this PDMS shown previously in Chapter 8. Besides, it also has a higher standard deviation. Thus, the preparation of this composite was not repeated due to the difficulty in the processing. The better performance shown here is most probably due to the uneven distribution of wood particles and PP plastic resulting in composite containing more than 30% plastic.

In addition, even though the particles still have a certain length, they are not fibres. Visible with bare eyes are the particles of an approximately 2-4 mm sizes in the composites' panels. They do not have ductility to absorb and restrain or transfer load effectively without self-breakage. On one hand, their particle size is not small enough and on the other hand, maybe above the critical particle size for effective reinforcement. That is why they do not reinforce but decrease the composites mechanical properties. The smaller particles in the wood flour have higher surface contact area with the polypropylene matrix hence increasing the interactions between the interfaces. So, the best performance among the three composites system could be seen from the composites filled with wood flour when more wood was used (Figures 9.2 – 9.4) and no significant difference when more plastic was used in the system (Figures 9.5 – 9.7). The following Figure 9.8 shows the composite panels with different particle size of wood.

Obviously with more wood composition, both PDMS and MAPP treatments have improved the mechanical properties of the composite with bigger wood particles although their properties were still lower than the composites containing wood flour. The mechanical properties of PDMS treated composites improved only slightly except with the longest particle size (as stated previously). This is because in this study 50% master batch of very high molecular weight bifunctional triethoxy-vinyl PDMS compounded in PP (BPP) was used. As discussed earlier in Chapter 8,

the BPP was not so effective in coupling the composite although these results still show that the treatment has improved the adhesion. The results also show that the higher surface area for interaction between wood and coupling agent or matrix is needed in enhancing the mechanical properties of the composites filled with wood particles.



Figure 9.8: WF/PP 70/30 panels with 1.75% very high molecular weight bifunctional triethoxy-vinyl PDMS (a) with particle size of 0.3 – 0.5 mm and (b) with particle size of 0.6 – 1.25 mm

9.1.2 Water absorption

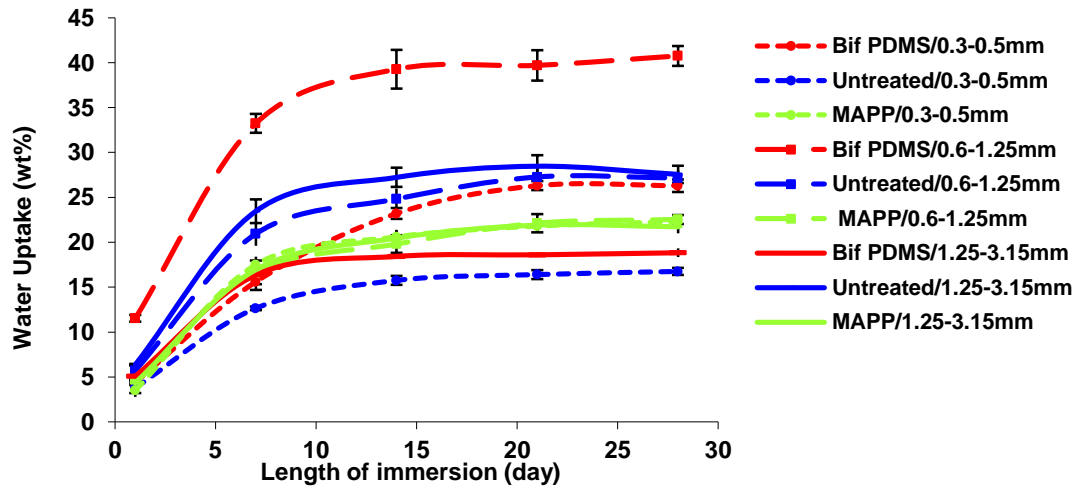


Figure 9.9: Water absorption of 70/30 WF/PP with or without 1.75% MAPP or very high molecular weight bifunctional triethoxy-vinyl PDMS (Bif PDMS) coupling agent in the composites containing different particle size of wood.

From Figure 9.9, we can also see that, when 70% of wood was used, the water absorption of the untreated composites increases with the increasing of particle size. The MAPP treatment caused no significant effect on the water absorption

regardless of the particle size and PDMS caused highest water absorption with middle particle size (mid-WP) and lowest with long-WP in comparison with the wood flour. In addition, we can also see from the Figure 9.10 that the volume change of the composites with or without coupling agent using the smallest particle size is better compared to the bigger particle sizes.

Theoretically, the smaller the particle size the more water will be absorbed due to the higher surface area per unit weight (Ashori & Nourbakhsh, 2010). However, the untreated composites analysed in this study show contrary results. This is due to the particles' breakages producing new various sizes and shapes of particles, thus causing an uneven distribution of particles, which leads to the existence of gaps and voids in between the different shapes' particles in the composites. According to Das *et al.*, (2000), there are three main regions where the adsorbed water in the composite can reside: the cell wall, the lumen (via porous tubular), and the voids between lignocellulosic material and PP in the case of weak interface adhesion. We can see from the flexural strength of untreated composites that the bigger particles' composites have poorer interface adhesion. Thus, we can deduce that composites with the smallest wood particles are dimensionally more stable in terms of volume change.

Composites treated with MAPP seem not to be influenced by the size of wood particles, probably due to the better interaction existing between wood and PP. The composition of plastic in the composites with bigger particle size did probably not much alter due to uneven flow during processing showing only a slight difference compared to the original 70% wood amount. PDMS treatments with the smallest particles are better because of better interaction with wood flour of uniform size and shape, while the long-WP composite shows better performance because of the higher composition of plastic. The higher water absorption in the mid-WP composite should originate from the gaps and voids at the interfaces, what increases the tendency to absorb water. Water absorptions of both treatments are still higher than of the untreated wood flour composite as discussed earlier in Chapter 7.

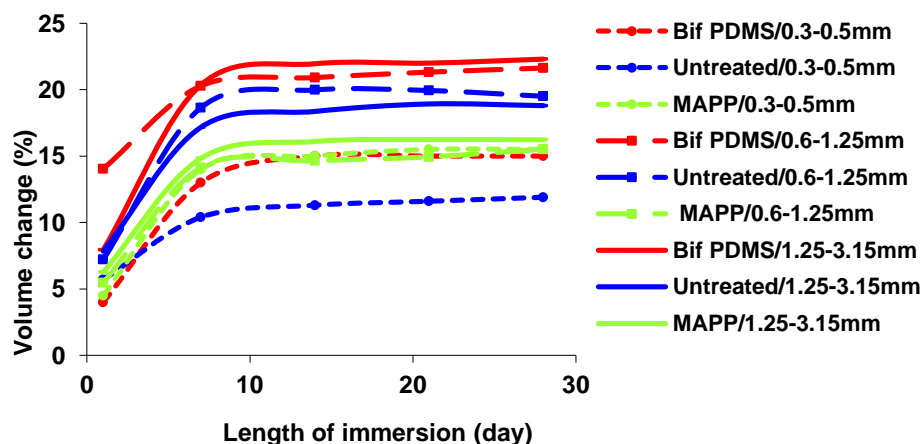


Figure 9.10: Volume change of 70/30 WF/PP with or without 1.75% MAPP or very high molecular weight bifunctional triethoxy-vinyl PDMS (Bif PDMS) coupling agent in the composites containing different particle size of wood.

9.2 The effect of re-compounding on the properties of WF/PP composites

Re-compounding the treated composites of both very high molecular weight bifunctional PDMS by impregnation procedure and MAPP treatments have been made for two reasons. First, we assumed that the retention time in our compounder is too short to allow full reaction of coupling agent during processing. For that reason, we would like to see if a longer retention time by re-compounding could further propagate the unfinished coupling agent reaction. The second is to see the composites' performance after being processed for the second time as for example during recycling the product. It was done by grinding the composites to the pellet form and running them through the compounder for one more time under the same processing conditions. The following Figures 9.11 to 9.17 show the results.

9.2.1 Mechanical properties

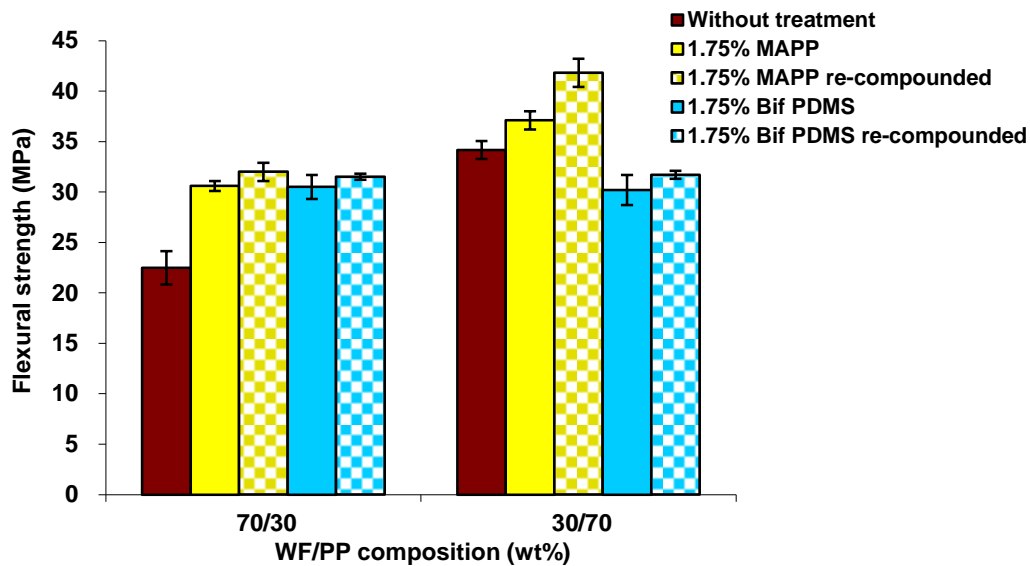


Figure 9.11: The effect of re-compounding of the treated composites with different composition to the flexural strength

On one hand, the flexural strength (Figure 9.11) of the re-compounded MAPP treated composites with 70% plastic has increased, while the re-compounded PDMS treated composites have not significantly changed or show only slight increments after the second processing. On the other hand, the modulus of elasticity of composites with more wood decreased (Figure 9.12) while the composites with more plastic has not significantly affected. The re-compounding results are also connected with a lower standard deviation, especially with PDMS treated composites. The results are comparable to the original composite as we can see in Table 9.1: the density of the tested specimens of one time compounded composites and the two times processed are about the same.

From these results, we can say that further interactions have occurred between the MAPP coupling agents and the PP-wood interfaces, improving the

adhesion. More plastic ensures better encapsulation of the matrix resulting in better mechanical performance compared to the 70% wood composites. Impact strength also increased due to the better interaction existing in MAPP re-compounded composites containing more plastic (Figure 9.13).

Re-compounding might have caused particle breakage due to increased shear stress from particle-particle, particle-screw and particle-barrel interaction during the second processing, decreasing the stiffness of the composites. However, with more plastic in the composites, no significant effect of re-compounding was observed on the modulus of elasticity. This should be due to lower composition of wood in the composites, avoiding additional shear stress from the re-processing.

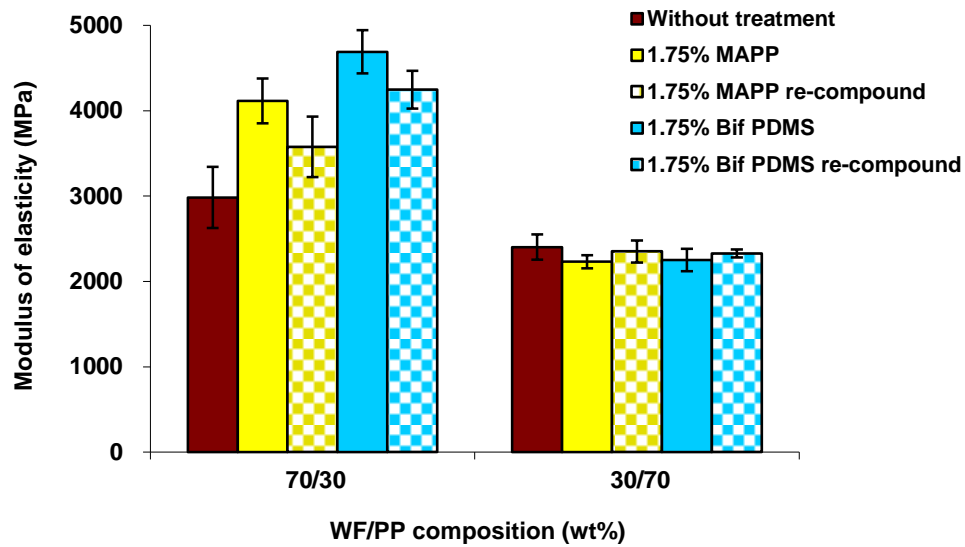


Figure 9.12: The effect of re-compounding of the treated composites with different composition to the modulus of elasticity

Table 9.1: Density of flexural test treated composites specimens

Composites condition	Density for different formulation -WF/PP/coupling agent (kg/m ³)							
	70/30/1.75 MAPP (%)		30/70/1.75 MAPP (%)		70/30/1.75 PDMS (%)		30/70/1.75 PDMS (%)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Original	1.16	0.07	0.97	0.08	1.18	0.02	0.96	0.07
Re-compounded	1.14	0.09	0.97	0.09	1.17	0.01	0.97	0.06

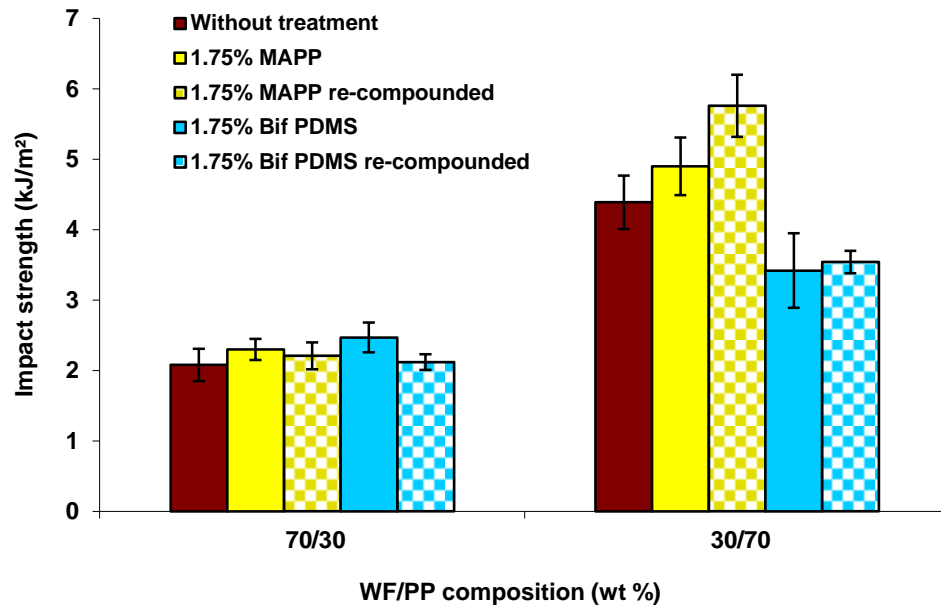


Figure 9.13: The effect of re-compounding of the treated composites with different composition to the impact strength

9.2.2 Water absorption

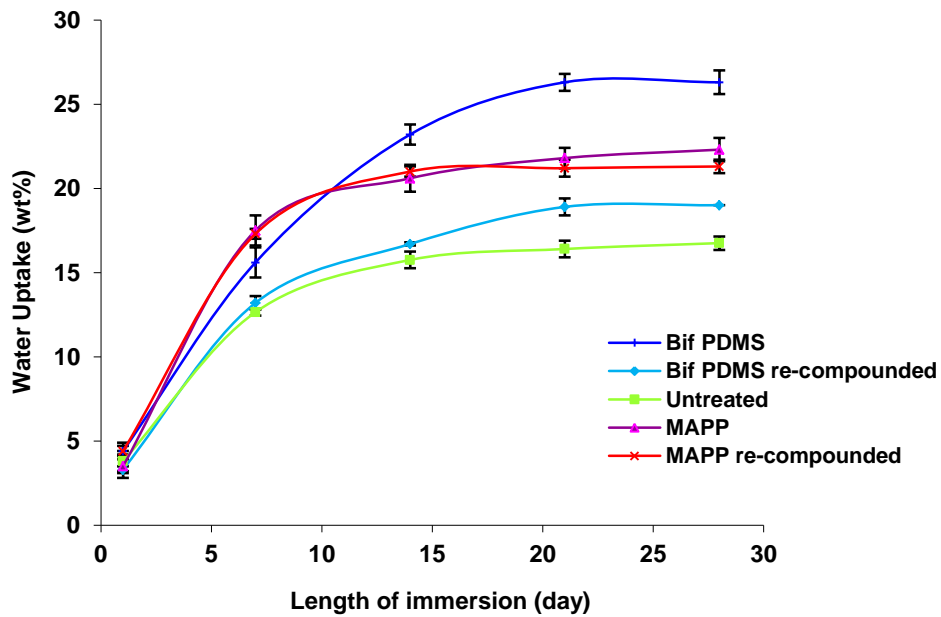


Figure 9.14: The effect of re-compounding of the 70/30 WF/PP composites with different treatments on the water absorption.

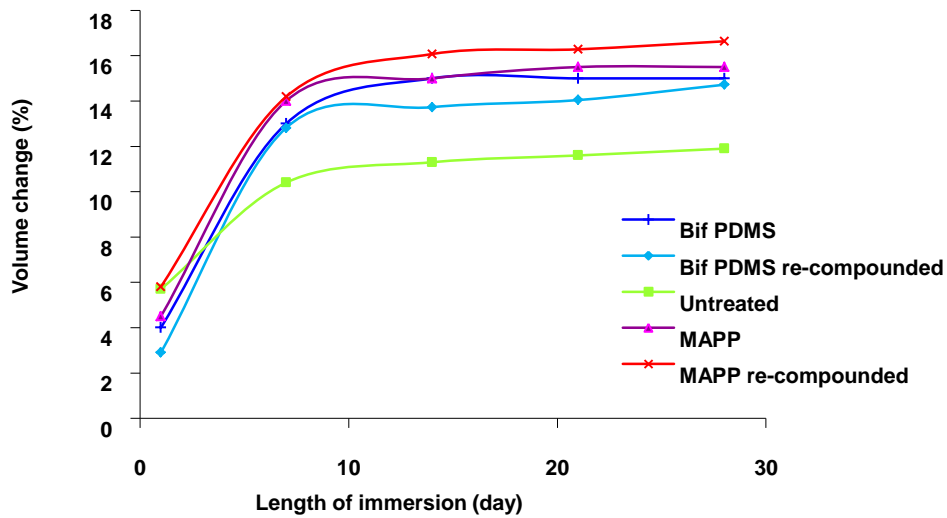


Figure 9.15: The effect of re-compounding of the 70/30 WF/PP composites with different treatments on the volume change.

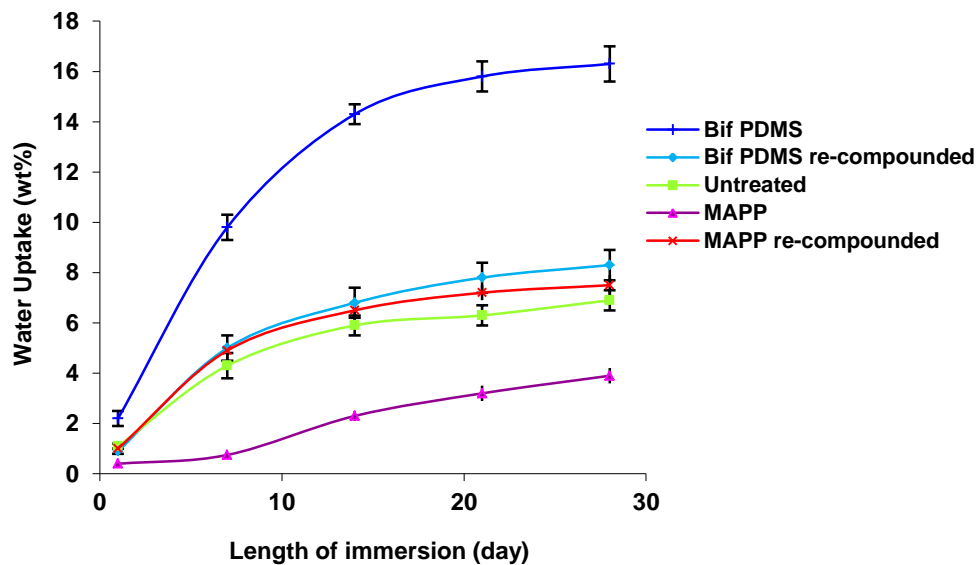


Figure 9.16: The effect of re-compounding of the 30/70 WF/PP composites with different treatments on the water absorption.

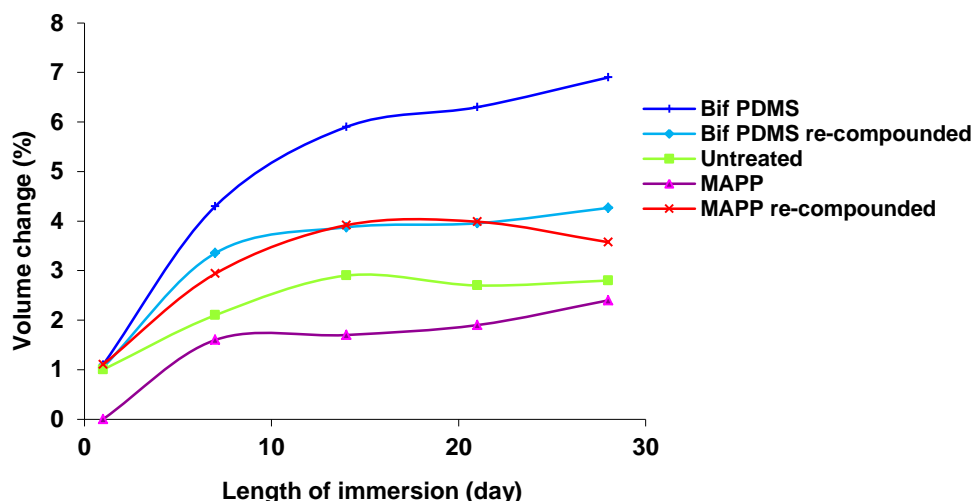


Figure 9.17: The effect of re-compounding of the 30/70 WF/PP composites with different treatments on the volume change.

The water absorption and composite stability have improved with the re-compounding for both 70/30 and 30/70 compositions of PDMS treated composites (Figures 9.14 – 9.17). However, the improvements are still lower or just about the same as for the untreated composites. These improvements might be due to better dispersion of coupling agent after re-compounding. The hydrolysed sugar might also have reacted during re-processing leaving less free –OH groups in the composites thus decreasing the water absorption.

Re-compounded MAPP treated composites with more wood shows insignificant differences on water absorption compared to the original MAPP treated composites. The re-compounded composites with more plastic absorb more water, what is expected to be due to the hydrolysis of the formed ester bonds because of their small number as also stated by Danyadi *et al.*, (2010) and discussed earlier in Chapter 7.

After all, the re-compounding process does not alter too much of the mechanical properties but improves the water absorption of the composites treated with PDMS. It also improves the strength of the MAPP treated composites with more plastic but caused more water absorption.

9.3 The effect of MAPP pre-mixing on the properties of WF/PP composites

Pre-mixing was done in the first place to distribute the MAPP before compounding. That is because there were only two feeding systems to feed the materials at a time. So, in order to introduce a third component, pre-mixing is needed with one of the main components. MAPP was delivered in pellet form allowing a pre-mixing with the PP. The pre-mixing was done in a thermo mechanical mixer as described in Chapter 3, section 3.2.2. However, considering the different reactions might have occurred if pre-mixing was done with wood, another investigation was made to confirm the possible effect.

9.3.1 Mechanical properties

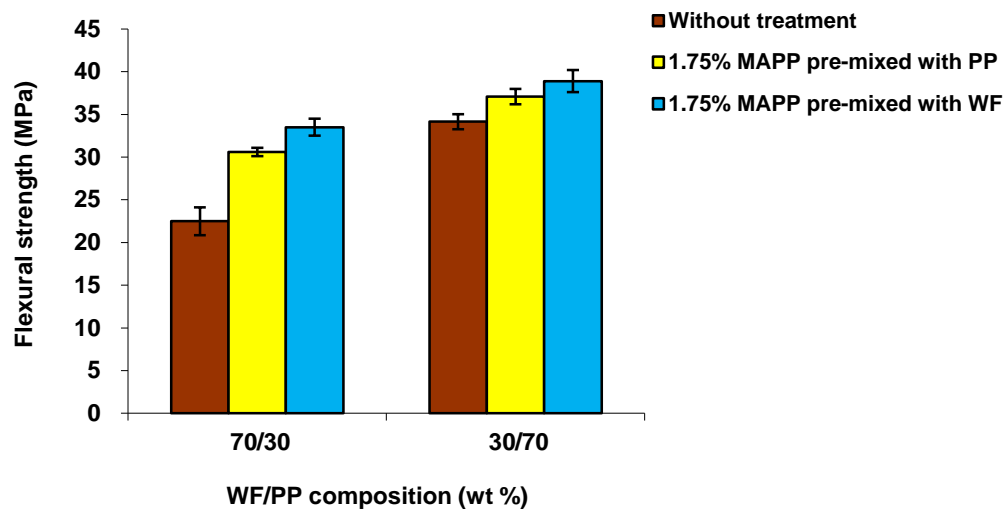


Figure 9.18: The effect of MAPP pre-mixing to the flexural strength of composites with different compositions

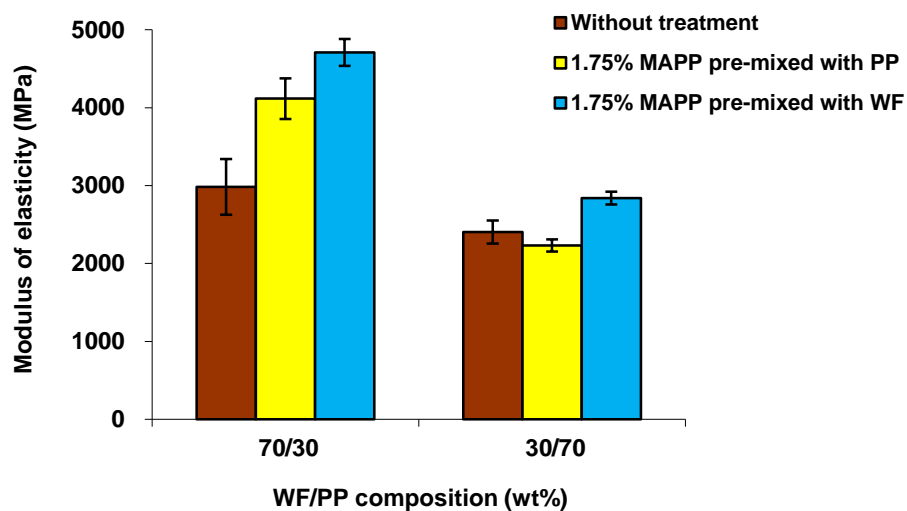


Figure 9.19: The effect of MAPP pre-mixing to the modulus of elasticity of composites with different compositions

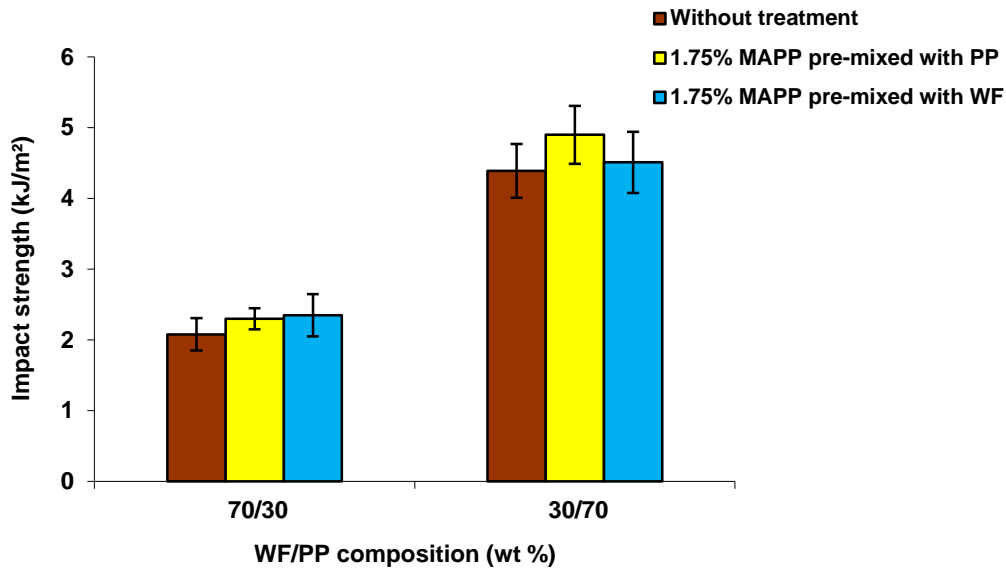


Figure 9.20: The effect of MAPP pre-mixing to the impact strength of composites with different composition

From the results (Figures 9.18 to 9.20), it is obvious that the flexural strength and the modulus of elasticity are improved when pre-mixing was done with wood for both compositions of composites. However, the impact strength did not really alter for composites with more wood and decreases with higher amounts of PP.

These results show that better interaction between MAPP and wood would exist when more retention time was given, which might be achieved through pre-mixing or through compounding. More ester linkages might have occurred in the wood performing better bridging at the wood-PP interfaces. The surface energy of the wood might have increased to a level much more closely to the surface energy of the matrix (Bledzki *et al.*, 1996) giving better wettability and a higher interfacial adhesion. According to Hill (2006), cellulose fibres can react with pre-heated MAPP always better than with as-received MAPP. Their FTIR studies have shown that there was a higher level of ester linkages when the composites were produced using the pre-heated MAPP.

9.3.2 Water absorption

Water absorption and volume change (Figures 9.21 to 9.24) also show better performance with pre-mixing of wood flour compared to pre-mixing of PP. These results confirm that less free –OH groups exist in the composites that might be due to higher level of ester linkage formation thus reducing water absorption.

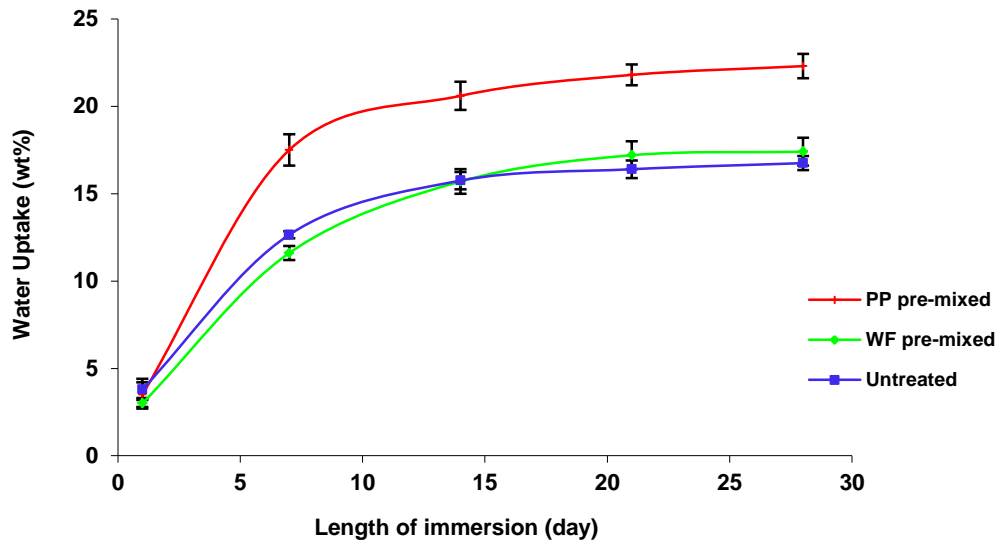


Figure 9.21: The effect of 1.75% MAPP pre-mixing to the water absorption of 70/30 WF/PP composites.

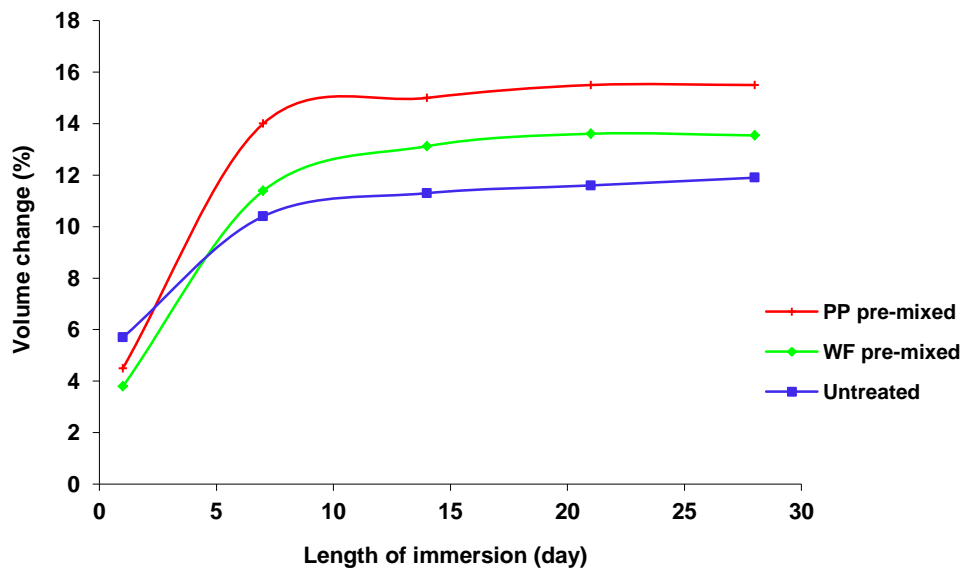


Figure 9.22: The effect of 1.75% MAPP pre-mixing to the volume change of 70/30 WF/PP composites.

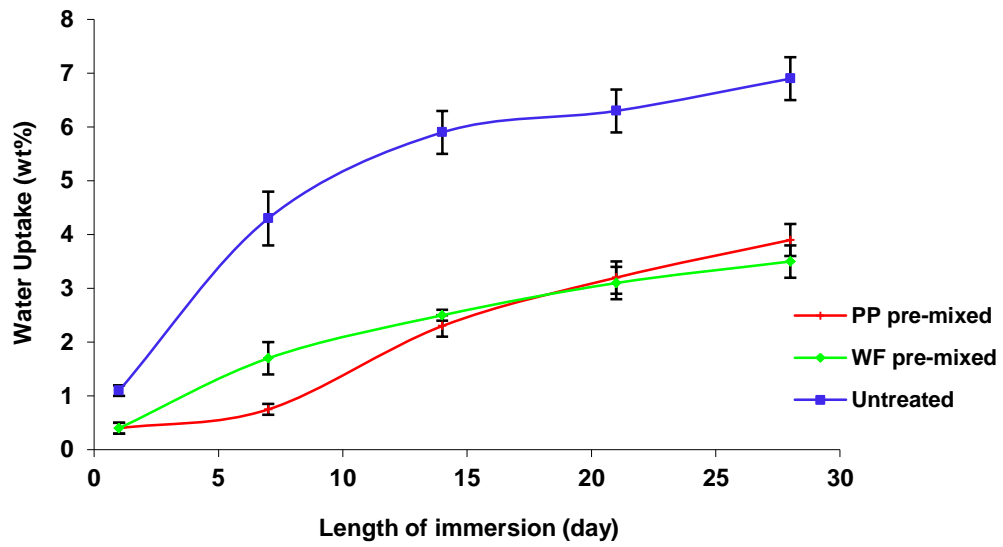


Figure 9.23: The effect of 1.75% MAPP pre-mixing to the water absorption of 30/70 WF/PP composites

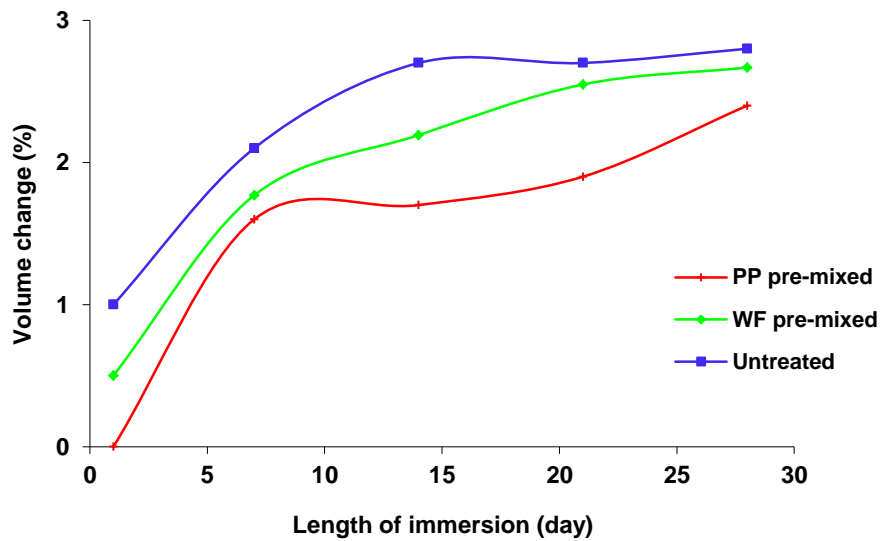


Figure 9.24: The effect of 1.75% MAPP pre-mixing to the volume change of 30/70 WF/PP composites

10 Conclusions

The studies in this doctoral thesis concentrate on a special formulation of WPC in a special lab compounder equipment. The results show that the mechanical properties of WPC containing 70% of wood flour and 30% PP can be successfully enhanced by coupling reaction with very high molecular weight bifunctional triethoxy-vinyl PDMS and with DCP as the radical initiator. The enhancement was achieved with only 1.75% coupling agent to the weight of wood flour by vacuum impregnation procedure with 88% mass uptake recorded. The existence of coupling agent in the wood flour could be seen in the FTIR spectrum and has decreased absorption of moisture during storage by around 40%.

1.75% coupling agent has proven to be enough to compound the hydrophilic wood flour with the hydrophobic PP. Too much coupling agent only acted as plasticizers, making the composites more flexible and decreasing the flexural strength and modulus of elasticity. On the other hand, too little coupling agent was not enough to strengthen the composite and works as an impurity in the composites. 0.1% DCP has effectively initiated the radical reaction and is believed to have coupled the vinyl group in the bifunctional PDMS to the PP, thus bridging the coupling agent at the wood-PP interfaces when triethoxy at the other end of the coupling agent might have covalently bonded to the wood during impregnation. An interphase of coupling agent was believed to exist at the interface of wood and PP, but Si component from 1.75% of bifunctional PDMS was too little to be detected by SEM-EDX to perform chemical mapping and the proposed C-O-C covalent bonding could also not be detected by FTIR spectrum comparison. However, the treatment has increased about 35% of the flexural strength and 75% of the modulus of elasticity compared to the untreated composites. The impact strength results also show some increment. The activation energy (E_a) calculated by depicting the Arrhenius-plot of the composites from the maximum temperatures of the loss tangent (T_g) at the different frequency from DMA analysis also shows an increment with the treatment. The treated composites have higher E_a of the glass transition temperature, which is 371 ± 3 kJ/mol compared to the untreated composites 301 ± 1 kJ/mol.

The composite containing bifunctional groups of vinyl and triethoxy attaching to the coupling agent performed better with 20% higher in flexural strength and 25% higher in modulus of elasticity comparing to the composite containing a mixture of both vinyl and triethoxy single functional group with the same amount of treatments and composites preparation. The activation energy (E_a) of the glass transition temperature is also by 38% higher, showing that better adhesion has obtained when the functional groups were covalently attached to the PDMS backbone. Among the bifunctional triethoxy-vinyl PDMS with different molecular weight, the one with the highest molecular weight was much more effective in adhering and wetting the interfaces of the composites that might be due to the existence of longer mobile chain length, resulting in more molecular entanglement and increasing secondary van der Waals interactions.

The performance of composites treated with very high molecular weight bifunctional triethoxy-vinyl PDMS was also comparable with the performance of industrially established MAPP coupling agent. The flexural strength was more or less the same but the stiffness was about 20% higher and with only 3.6% difference in the activation energy. Overall, we can optically see the microstructural quality of the bifunctional PDMS treated composites being homogenous with good wetting and voids hardly detectable. However, even though the mechanical properties were improved, the water absorption of the treated composites also increased. The 70/30 WF/PP composites treated with the commercial MAPP as well shows the same results. Processing with the small extrusion compounder is believed to be one of the causes, due to the very low retention time during compounding, that has hindered some of the coupling agent to react completely. Hydrolysis was believed to occur in the composites. Hydrolysis of the formed ester bond might have occurred with MAPP treatment and hydrolysis of polysaccharides occurred in the bifunctional PDMS treatment. Both lead to increase the free OH-group in the composites that tend to absorb more water compared to the untreated composites. The sugar analysis has proven that the treated composites contained 48% more free sugar.

Treatment of the wood by vacuum impregnation with PDMS solution was found to be the most effective way of applying the very high molecular weight bifunctional triethoxy-vinyl PDMS compared to the surface spraying of PDMS emulsions or direct compounding the ready compounded PDMS-PP. This seems to be due to longer contact time between the wood and PDMS has led to a better reaction.

A loading of 70% of wood flour into the PP with good adhesion could reduce cost and increase use of the WPC. However a ratio of 50/50 WF/PP composition was found to give better characteristics. Depending on the field of use the bifunctional PDMS treated composites composition could be tailored to give better performance. They could also be reprocessed without loss of the performance and characteristic moreover improving water absorption.

Further investigation should be done to investigate the effectiveness of very high molecular weight bifunctional triethoxy-vinyl PDMS as coupling agents in WF/PP composites. The following study is suggested for further understanding on the role-plays by this coupling agent in bridging the composites' interfaces:

- The effect of pH value on the coupling reaction. In which condition the coupling reaction could be controlled?
- The effect of different processing conditions in producing WF/PP composites. What happen if the composites are produced using a bigger scale extrusion compounding process? Will the same characteristics remain?
- The effect of bifunctional PDMS coupling reaction on the hydrolysis of polysaccharides in wood and the relationship between the hemicellulose content to the amount of free sugar in the composites. What factors contribute to the hydrolysis reaction and what is the critical limit to avoid hydrolysis?

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Appendixes

Appendix 1: The solvent solution to w/w% treatment conversion calculation

1% solution means 1g of solute dissolved to a final solution of 100ml. Every kg of wood flour needs 3.5 liters of solution for impregnation and every impregnation will be done with 2 kg of wood flour. So for every 2 kg impregnated wood flour the conversion to w/w% treatment is as follows:

When 0.5% coupling agent solution was used, the 100ml final solution will contain 0.5 g of solutes and in 3 500 ml solution will contain $0.5 \text{ g} \times 3500 \text{ ml} / 100 \text{ ml} = 17.5 \text{ g}$ solutes.

2 kg wood flour needed 7 000ml of solution for impregnation. So the amount of solutes used was 35 g. So the w/w% coupling agent treatment is equalled to: $35 \text{ g} / 2000 \text{ g} \times 100 = 1.75 \text{ w/w\%}$.

Appendix 2: Contact angle and surface tension

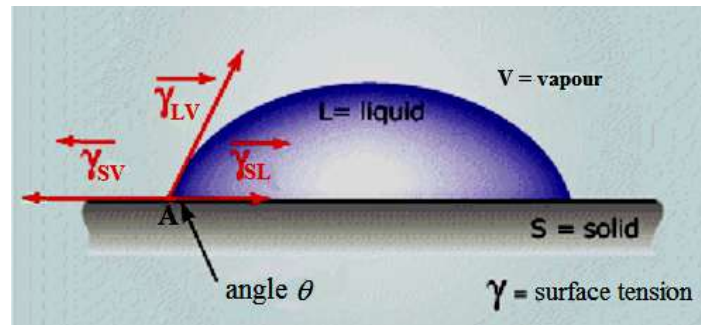


Figure A2.1: Contact angle (θ) and surface tension (γ) of liquid drop on a solid surface. SV, SL and LV stand for solid-vapour, solid-liquid and liquid-vapour interface respectively (Hull, 1995).

The physical situation of a liquid drop on a solid surface (Figure 2.25) can be used to understand the wetting process. When a drop of liquid is placed on a horizontal solid substrate, three boundaries meet around the profile of the drop: solid-vapour interface, solid-liquid interface and liquid-vapour interface. It is generally described using Young's equation when the forces at a point A are resolved in the horizontal direction; the Young's equation states:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \quad \text{Equation A2.1}$$

where γ_{SV} , γ_{SL} and γ_{LV} are the surface free energies or surface tensions of solid-vapour, solid-liquid and liquid-vapour interfaces respectively and θ is the contact angle.

Ideally, for a spontaneous wetting to occur θ should be zero. For systems where θ is high, more work is necessary to penetrate and wet out the solid surface. From Equation 2.1 we can indicate that θ can be reduced and wetting improved in three ways that are by raising γ_{SV} or lowering γ_{SL} and/or γ_{LV} (Niska & Sanadi, 2008). The lower the contact angle is, the better the wetting. Another useful parameter in considering the wetting of solid surface is the concept of critical surface tension of wetting, γ_C introduced by Zisman. The concept states that only liquid with $\gamma_{LV} < \gamma_C$ will spontaneously spread on the solid (Hull, 1995).

The relationship between wetting and adhesion can be understood by combining of the Young's equation with the work of adhesion equation, W_A . Dupre developed W_A for calculating pull-off work associated with separating a liquid from a solid substrate (Piao *et al.*, 2010). It states that:

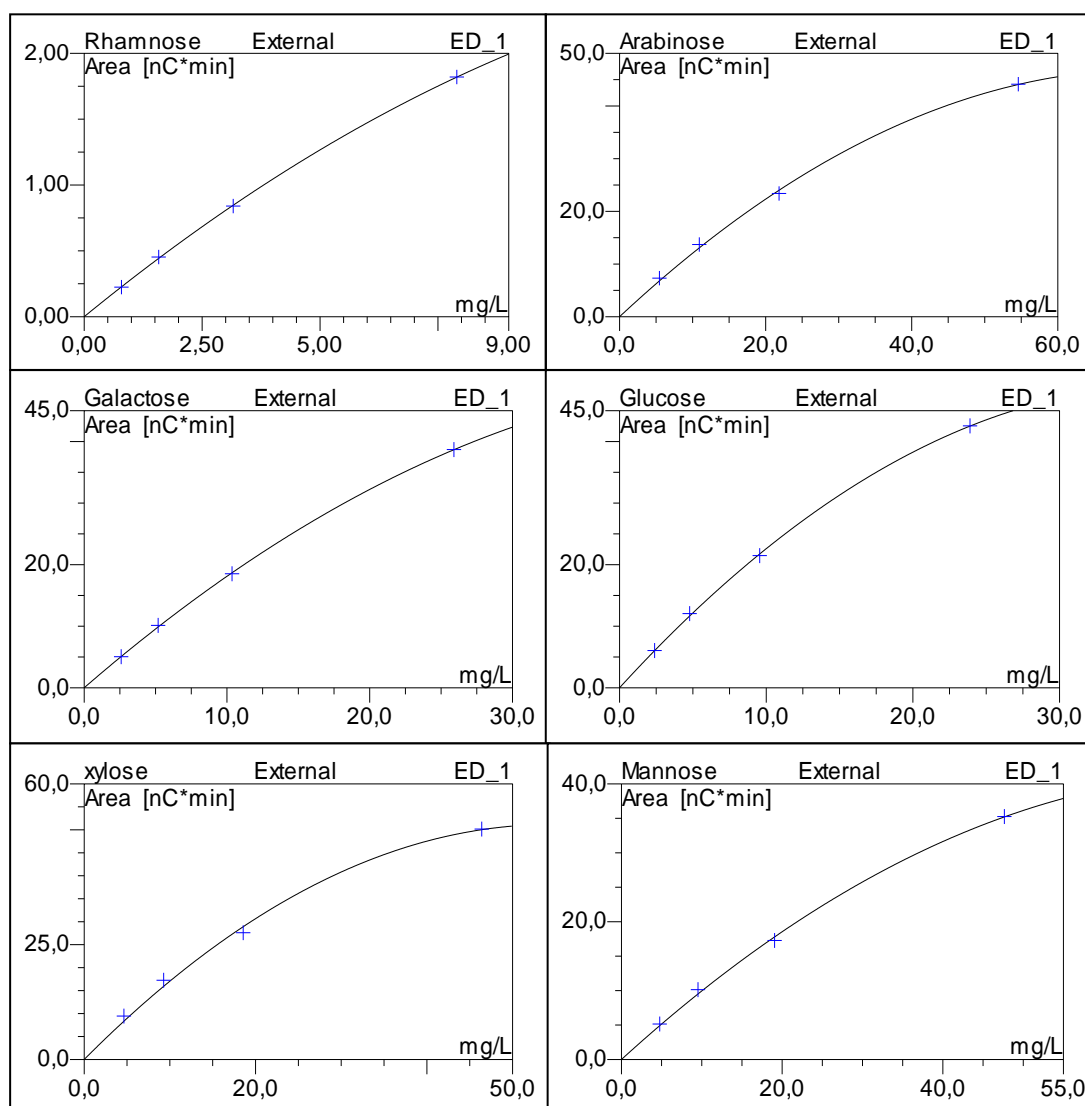
$$W_A = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \quad \text{Equation A2.2}$$

The combination equation gives:

$$W_A = \gamma_{LV} (1 + \cos \theta) \quad \text{Equation A2.3}$$

W_A is maximized when θ is zero and will be lower if the wetting is poor since the interfacial is reduced. Young's equation is applicable to an ideal surface, which is flat, perfectly smooth, rigid, topographically and chemically homogenous, nonreactive, insoluble and not perturbed by chemical interaction or by vapour or liquid sorption (Piao *et al.*, 2010). However, these equations can be used as a guideline to understand the relationship of wettability and surface tension and work done by adhesion. Wettability and contact angle are inversely related; the lower the contact angle, the greater the wettability, which means also the greater the work of adhesion.

Appendix 3: Calibration plot of every free sugar with four points standard solutions



Curriculum vitae

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PERSONAL DETAILS

Gender: Female
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EDUCATION BACKGROUND

2006 – 2012 (11 semesters): Technical University Braunschweig

- Ph.D. in chemistry
- Full time research at Fraunhofer, Wilhelm-Klauditz-Institut für Holzforchung

2000 – 2002 (5 semesters): National University of Malaysia, Bangi, Selangor

- Master of Science (Chemistry), Full time research
- Research project: Processing of NR/LLDPE/Twaron composite using a twin screw extruder

1997 – 2000 (6 semesters): National University of Malaysia, Bangi, Selangor

- Bachelor of Science, Second class Honours (Upper division)
- Field of Study: Chemical Technology, Final year project: Vulcanization of NR/LNR with sulfur

WORKING EXPERIENCES

Dis 2005 – Sept 2006: National University of Malaysia

- Lecturer at Faculty of Science and Technology

July – Dis 2005: National University of Malaysia

- Tutor at Faculty of Science and Technology

July 2003 – July 2005: Technology University of Malaysia

- Lecturer at Military Academy Malaysia

Feb – July 2003: National University of Malaysia

- Research assistant at Faculty of Science and Technology

ACHIEVEMENT/PUBLICATION

- Silver medal in the UKM Research and Innovation Exhibition 2003
- Ishak Ahmad, Norul Azwan Din, Affendi Mohamad, Azizah Abdul Aziz & Ibrahim Abdullah. 2005. Penambahan Gentian Aramid (Twaron) dalam Adunan NR/LLDPE dan ENR/LLDPE terhadap sifat Mekanik Komposit. *Sains Malaysiana* **34(1)**: 57-61
- Ishak Ahmad, Azizah Baharum, Mohd Khairil Saat & Ibrahim Abdullah, Kesan Komposisi Gentian dan Kaedah Pemprosesan ke atas Sifat Mekanik Komposit NR/LLDPE Diperkuat Twaron, *Sains Malaysiana* **33(2)** 2004: 9-19.
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